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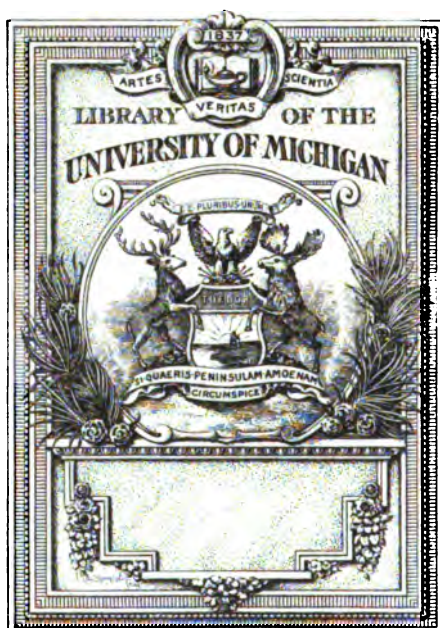
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THE
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THE

Journal of Analytical AND Applied Chemistry.

CHARACTERISTICS OF WELL AND SPRING WATERS IN A THICKLY POPULATED AREA.

BY CLIFFORD RICHARDSON.

The District of Columbia has at present about two hundred and seventy (270) wells and springs, most of which, in addition to its aqueduct, are in public use as sources of water supply by a large number of people. An experience of three years in the examination of the waters from these wells and springs has led to the collection of a large number of analyses, which furnish some interesting data illustrating the effect of the density of population in different areas upon their quality, and also the value of local standards of purity in interpreting the results of any particular analysis.

These wells are, with a few exceptions, shallow, averaging about thirty (30) feet deep. They are supplied in some cases by flowing springs, and in others only by ground water, but all are much influenced by the latter, and as they are not ceiled up in a water-tight manner, receive varying amounts of storm water leaching through the surface soil. They are subjected, therefore, to the following sources of contamination :

Oxidized products of filth from soil, which has supported a comparatively dense population for many years, carried into the wells or springs by the leaching process.

Direct sewage contamination from improper sanitary arrange-

ments, or from adjoining sewers, forming part of our sewage system.

Storm water carrying in surface filth.

Roots of trees reaching the well.

Dripping back into the wells of water from the pumps.

The methods employed have been practically those recommended by Leffman and Beam in their valuable compendium of methods of water analysis recently published. Of them it seems necessary to say nothing, except, that owing to the large number of analyses made, the work has been very thoroughly systematized, and the errors creeping into scattered and occasional work, I hope, entirely eliminated. The "oxygen consumed" represents that derived from permanganate in ten minutes at the temperature of ebullition.

The analyses number four hundred and sixty-six (466), representing two hundred and twenty-three (223) wells and springs, which have been classed as :

1. *Passable*: Those in which the nitrogen as nitrites does not exceed .005 parts per million, or in which there is no other evidence of gross or dangerous contamination, as shown by large amounts of nitrogen in other forms, of chlorine or of oxygen consumed, or by a combination of results. The wells of this class are some of them by no means of the best character, but are not apparently unsuitable for use in the light of the environmental evidence and of our experience, and apparently cannot be safely condemned on the undecisive figures of the chemical analysis alone.

2. *Suspicious or Contaminated*: Those containing more than .005 parts per million of nitrogen as nitrites showing contamination in an active state of oxidation, and those in which the joint evidence of the other determinations is plainly condemnatory.

3. *Individual wells and springs*, the study of which extends over a considerable period of time.

The former classes were subdivided in accordance with the different sections into which the District is divided, namely, the Northwest, Northeast, Southwest, and Southeast from the Capital as a centre, and the County being that part of the District out-

side the immediate city limits, Georgetown, as on old and thickly populated portion, being included in the Northwest section.

The Northwest section has supported the largest and densest population for the longest time. The Northeast is less thickly settled, and in parts very sparsely. The Southwest is quite densely populated, and has the additional peculiarity of including the low area on the river front, much of the soil not far below the surface revealing a swampy origin. The Southeast is higher, but not as far from the river or Eastern branch as the Northeast and Northwest, is rather thickly settled in some portions, but not in others, and has supported its population for a much shorter time as a whole than the Western sections. The County includes the higher river terraces and also the outlying low land of the Eastern branch of the Potomac, and has soils of very different nature at different points. A map of the District will give a fair idea of the lay of the land to those unacquainted with the locality.

Following are the results obtained :

CHARACTERISTICS OF WELL AND SPRING WATERS.

Passable Wells.

RESULTS IN PARTS PER MILLION.

Serial No.	LOCALITY.	Date.	Condition.	Color.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrates.	Chlorine.
	<i>County.</i>	1888.									
118	1/4 mile out Bladensburg road	Oct. 10	Turbid	Ferruginous	73	.040	.040	.90	trace	trace	16.0
120	Glenwood road.	85	.020	.036	.16	.001	6.0	15.5
154	Brentwood school	104	.008	.034	.32	.000	1.0	17.5
190	Elverson's, Georgetown.	99	.100	.104	1.38	.000	4.0	10.0
1144	Industrial H. school	Aug. 26	Clear	88	.004	.012	.24	.000	5.6	17.5
		1889.									
1535	" "	Dec. 31	"	Yellow tinge	30	.024	.100	1.18	.000	.0	4.5
1734	" "	April 24	"	176	.000	.124	1.96	.000	trace	47.5
1615	35th and new cut road	Mar. 11	"	286	.048	.100	.22	.000	16.0	46.0
2184	Columbia Heights	July 16	"	142	trace	.020	.76	.000	1.0	26.3
2222	Woodley lane	July 22	Slightly opal	174	.000	.020	.22	.000	0.0	4.0
2228	Monroe street, Anacostia	Aug. 13	"	274	.000	.064	.38	trace	15.0	44.5
2342	Hillsdale. . . .	Aug. 19	"	Light straw	68	.000	.140	.32	.000	trace	13.0
2540	Fort Myer*. . . .	Oct. 8	Clear	72	.000	.212	.16	.020	2.8	16.0
2865	Klingie Ford. . . .	Dec. 31	"	76	.060	.140	3.12	trace	trace	3.0
		1890.									
3229	Brightwood	July 2	"	108	.008	.072	.32	.000	3.0	12.5
3384	Georgetown	Aug. 26	"	30	.142	.160	1.56	trace	0.5	2.4
	Average.	118	.028	.086	.83	.001	3.2	16.0

*Driven wells.

Passable Wells.—Continued.

Serial No.	LOCALITY.	Date.	Condition.	Color.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	<i>Southeast Section.</i>	1888.									
830	6th and B streets	June 26	Clear	266	.004	.024	.28	.000	15.0	83.5
997	17th and Massachusetts ave. .	Aug. 14	Cloudy	Yellow	174	.000	.008	1.82	.000	6.0	26.3
		1889.									
1568	3rd and South Carolina ave. .	Feb. 18	Turbid	"	278	.060	.148	.90	.000	18.0	52.5
1859	3d and Pennsylvania ave. . .	May 20	Clear	246	.020	.121	.90	.000	18.0	74.0
2246	4th and E streets	July 29	"	300	.008	.092	.50	.000	15.0	92.0
2287	4th and East Capitol	Aug. 13	"	190	.000	.032	.32	.000	.8	43.0
2420	3d and M	Sept. 17	"	438	.000	.112	.28	.005	8.0	41.5
2461	4th and North Capitol . . .	Sept. 23	"	295	.008	.020	.24	.000	25.0	39.0
2535	1st and O	Oct. 7	"	238	.146	.168	.70	trace	3.0	59.0
2567	"	Oct. 14	"	246	.100	.260	.50	.000	trace	59.5
2863	1st and M	Dec. 31	Milky	376	.060	.052	.66	.005	6.0	91.0
		1890.									
3003	Washington Asylum	Mar. 17	Turbid	134	.020	.060	.10	trace	.0	11.5
3004	17th and Georgia ave. . . .	Mar. 18	Clear	162	.192	.112	.42	trace	12.0	32.5
3029	North Capitol, bet. 1st and 2d	April 1	"	360	.200	.152	.70	trace	25.0	74.0
3139	17th and A	May 20	"	163	.020	.100	.44	.005	8.0	24.0
3232	12th, bet. D and E	July 2	Org. Odor	376	.020	.072	3.08	.000	12.0	69.5
3254	6th and B	July 15	"	370	trace	.040	.26	.000	8.0	57.5
3398	9th and South Carolina ave. .	Aug. 20	Clear	336	.001	.141	.36	trace	6.0	47.5
3456	4th "	Aug. 23	Sl. cloudy	211	trace	.240	.36	trace	8.0	37.5
3470	8th and A	Aug. 30	Clear	260	.020	.020	.46	trace	15.0	42.5
	Average	261	.044	.099	.67	trace	10.4	52.4

CHARACTERISTICS OF WELL AND SPRING WATERS.

Passable Wells.—Continued.

Serial No.	LOCALITY.	Date.	Condition.	Color.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrites.	Chlorine.
	<i>Northeast Section.</i>	1889.									
319	Delaware ave. and C street	Mar. 13	Clear	200	.048	.080	.72	20.0	.000	19.0
482	5th and A streets	Mar. 13	330	.008	.168	2.36	28.0	trace	44.5
		1890.									
2979	5th and A streets	Feb. 24	Clear	350	.048	.020	.24	28.0	.005	44.0
3200	12th and E streets	June 17	"012	.096	1.62	25.0	trace	24.0
3353	9th and A streets	Aug. 19	"	167	trace	.061	.22	5.0	trace	34.0
	Average	262	.023	.083	1.03	21.2	trace	33.1

Serial No.	LOCALITY.	Date.	Condition.	Color.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrites.	Chlorine.
	<i>Southwest Section.</i>										
1059	I between 4½ and 6th streets	Aug. 28	Turbid	Yellow.	566	.008	.048	.88	28.0	.000	111.0

Passable Wells.—Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	<i>Northwest Section.</i>	1887.	Clear	385	.005	.005	.29	.000	16.0	78.0
49	2nd and B*	Sept. 13	Clear	385	.005	.005	.29	.000	16.0	78.0
50	Q. between 13th and 14th	Sept. 13	"	209	.005	.045	.70	trace	20.0	30.0
62	St. John's College	Sept. 21	"	209	.040	.100	.35	.003	11.0	38.0
82	New Jersey ave., between M and N streets	Sept. 28	"	276	.005	.010	.52	.000	16.0	42.0
		1888.								
184	5th and L streets	"	"	275	.028	.040	.74	.003	.0	103.0
186	12th and Q streets	"	"	302	.008	.044	.88	.001	.5	110.0
399	E street and Virginia ave.	Feb. 13	"	265	.060	.040	.44	trace	15.0	51.5
669	12th street and Massachusetts ave.	May 15	"	292	.012	.120	.38	trace	18.0	52.5
829	7th street at Eastern Market	June 26	"	460	.008	.036	1.64	trace	38.0	66.5
868	6th and H streets	July 11	"	588	.004	.060	.26	.000	28.0	136.5
1098	10th and S streets	Sept. 11	Turbid	198	.008	.060	.48	trace	3.0	26.0
		1889.								
2264	10th and S Streets	April 5	Clear	196	.008	.088	.12	.000	6.0	27.5
1287		1888.								
1427	Rear of No. 2352 6th	Nov. 10	Sl. turbid	118	.000	.048	1.30	trace	8.0	17.5
	12th and New York ave.	Dec. 31	Clear	282	.008	.096	.30	trace	25.0	56.0
		1889.								
2030	Caroline street	June 25	"	106	.004	.060	.34	trace	4.0	13.8
2146	3rd and R	July 9	"	74	.008	.108	.90	.000	.8	9.3

Passable Wells. Northwest Section, Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrates.	Chlorine.
2265	4½, between B and C.	Aug. 5	Cloudy	368	.004	.100	1.04	.000	7.0	51.5
2379	New Jersey ave. and K street	Aug. 26	Clear	324	.000	.100	.18	trace	15.0	69.5
2538	12th and Boundary	Oct. 7	"	66	.008	.020	.22	.000	3.0	0.5
2598	5th and Ridge	Oct. 21	"	466	.012	.100	.50	trace	32.0	89.5
2723	Pound	Nov. 25	"	244	.004	.160	.76	.000	18.0	22.5
		1890.								
2895	New York ave., between 17th and 18th	Jan. 28	"	555	.060	.212	1.18	trace	28.0	91.5
2907	2306 6th	Feb. 4	"	144	.060	.204	1.08	.005	7.0	11.0
3231	3d and R.	July 2	"	168	.012	.060	.26	trace	8.0	17.0
3255	16th and Corcoran	July 15	"	186	.032	.072	.28	.000	2.0	26.0
3336	3d and L.	Aug. 12	"	411	trace	.100	.10	.000	15.0	63.6
3380	C and 1st	Aug. 26	"	131	trace	.060	.22	trace	5.0	18.0
3430	32d	Sept. 16	"	307	.001	.060	.16	trace	trace	7.5
	Average	274	.014	.079	1.56	trace	12.4	44.0

Suspicious or Contaminated Wells.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	<i>County.</i>	1887.	Clear	95	.120	.136	5.10	.018	2.0	19.0
119	Caton ave.	Oct. 10	"	222	.040	.068	.60	.025	13.0	50.5
123	Milk House Ford	Oct. 10	"	164	.032	.096	1.32	.030	6.0	20.5
124	Brightwood	Oct. 10	"	86	.020	.060	.32	.000	8.0	19.0
200	Brightwood, cleaned	Oct. 10	"	145	.032	.100	.36	.010	8.0	26.0
125	7th street, one-quarter mile out	Oct. 10	"							
		1888.								
908	7th street, No. 2700	July 24	Milky	174	.004	.068	2.08	.000	0.0	7.3
1363	T street, Hillsdale	Dec. 9	Very turbid	202	.360	.208	5.10	.000	0.0	37.5
1386	Brightwood	Dec. 12	Clear	140045	.28	.012	6.0	22.5
		1889.								
1766	Roanoke street, Columbia Heights	May 13	"	80	.032	.152	.48	.015	3.0	13.5
2144	Warner farm	July 9	"	116	.004	.124	.58	.020	2.0	33.0
2285	2454 7th street	Aug. 13	"	458	.060	.212	1.16	.300	18.0	64.0
2288	Harrison street, Anacostia	Aug. 13	"	92	.012	.100	.40	.032	3.0	19.0
2641	Sheridan avenue	Oct. 28	"	530	.012	.142	1.10	.015	45.0	87.5
2642	Howard ave.	Oct. 28	"	83	.140	.420	1.62	.140	2.0	15.5
2688	7th and Whitney ave.	Nov. 18	"	180	.104	.228	.98	.015	8.0	34.0
		1890.								
2868	Anacostia	Jan. 7	"	. . .	1.640+	.132	9.20	.875	large	39.5
2969	Superior street	Feb. 17	"	104	.142	.184	.42	.025	5.0	12.5
2970	Roanoke street	Feb. 17	"	148	.240	.908	2.70	.270	3.0	30.5
3228	Brightwood	July 2	"	243	1.760+	.972	large	.000	0.0	37.5
3383	Irvin street	Aug. 26	"	176	1.008	.340	2.64	.028	8.0	29.2
3415	Olivet street	Sept. 9	"	375	1.240	1.220	7.24	.000	0.0	77.5
	Average	191	1.37	.287	2.08	.087	3.6	33.1

Suspicious or Contaminated Wells. Southeast Section, Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrates.	Chlorine.
1749	Pennsylvania ave. and 3d	April 29	Clear ; org. odor.	248	.228+	.124	.78	.005	18.0	65.5
1857	7th, between G and L	May 20	Sl. turbid	1052	.108	.560	.90	.020	55.0	289.5
2378	9th, between G and I	Aug. 26	Clear	840	.004	.236	.50	.020	55.0	139.5
2459	1st and O	Sept. 23	Turbid	400	.060	.112	1.90	.300	4.0	113.5
3088	N, between N. J. ave and 1st	1890.								
3312	3d and C	April 29	Clear	612	.060	.162	.56	.008	18.0	159.0
3325	"	July 29	"	443	.020	.216	2.70	.005	28.0	109.0
3337	"	Aug. 5	"	360	.060	.264	2.38	.000	25.0	89.0
3397	"	Aug. 12	"	360	.048	.240	2.18	trace	15.0	84.5
3432	2d and C	Sept. 2	"	207	.020	.204	3.16	trace	5.0	34.0
3381	9th and South Carolina ave.	Sept. 16	"	90	.008	.320	.50	.005	3.0	36.0
3431	4th and South Carolina ave.	Aug. 26	Cloudy	322	.280	.060	.24	trace	18.0	55.2
		Aug. 16	"	220	2.000+	.280+	.30	trace	15.0	44.0
	Average	568	.305	.224	1.52	.022	24.6	104.0

Suspicious or Contaminated Wells.—Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrates.	Chlorine.
	<i>Southwest Section.</i>	1888.								
70	F, between Delaware ave. and North Capitol	Sept. 27	Clear	1096	.405	.170	Chalyb.	.005		174.4
151	B, between First and Second streets	1270	.264	.200	2.80	.600	6.0	165.0
1507	" " " "	1889. Jan. 21	928	.048	.220	.70	.018	45.0	106.0
555	Half street, between F and G	1888. April 3	Turbid	285	.420	.192	3.98	. . .	trace	32.0
619	Half street, between H and I	April 24	170	.392	.192	.90	trace	trace	43.0
1228	12th and C streets	Oct. 30	Sl. turbid	406	.120	.192	2.40	trace	23.0	98.0
1294	Four-and-a-half, between N and O streets .	Nov. 20	Clear	790	.080	.124	2.30	.058	35.0	187.5
1295	Four-and-a-half and F streets	Nov. 20	Turbid	690	.080	.212	3.72	.035	28.0	132.0
2118	" " " "	July 2	"	452	.008	.048	4.70	.100	15.0	111.3
2219	" " " "	July 22	Cl., sl. odor	476	.024	.140	.68	. . .	15.0	121.5
2343	" " " "	Aug. 19	"	500	.048	.204	.50	.012	8.0	119.0
1322	12th and E streets	Nov. 27	Sl. odor; turb	128	1.800+	.240	1.22	.068	8.0	24.5
1637	11th and F streets	1889. Mar. 18	Clear	1030	.012	.112	.64	.018	55.0	239.5
1729	Virginia ave. and 7th street	April 22	Turbid	426	.060	.100	3.12	.038	23.0	90.5
1933	3rd and L streets	June 4	"	524	.132	.100	.78	.060	25.0	167.8
1957	" " " "	June 11	Sl. turbid	550	.412	.100	1.50	.060	15.0	185.0
2117	Four-and-a-half and M streets	July 2	Turbid	540	.032	.160	1.16	.112	25.0	112.0
2218	" " " "	July 2	Sl. turbid	914	.104	.088	.90	.020	28.0	109.5
2145	Four-and-a-half, between C and D	July 9	Clear	306	.060	.132	1.12	.016	15.0	56.5
2221	6th and Maryland ave.	July 22	Sl. turbid	558	.004	.060	.54	.024	8.0	192.5
2568	1st, between N and O	Oct. 14	Clear	860+	.860+	.880+	1.24	.020	25.0	82.5
2597	14th and B	Oct. 21	"	324	.052	.112	1.10	.032	8.0	106.

Suspicious or Contaminated Wells.—Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
<i>Northeast Section.</i>										
257	312 K street	1887.048	.180	1.75	.020	27.0	145.0
400	8th and C streets	Nov. 15	Clear	560	.060	.072	.24	trace	55.0	96.5
875	16th street and Benning's	Feb. 14	Clear	224	1.032	.060	5.98	.950	2.0	28.8
936	2d and E streets	July 17	Cloudy	716	.012	.660	.26	..	48.0	92.0
1018	F, between North Capitol and First	July 31	..	1076	.460+	.400+	4.92	.038	3.0	278.8
1114	8th and A streets	Aug. 21	very turbid	174	.148	.124	.88	.018	5.0	23.5
1142	"	Sept. 18	Turbid	166	.060	.032	.22	.012	8.0	22.0
1115	"	Sept. 26	Milky	532	.060	.108	1.38	.038	28.0	86.3
1141	8th and Maryland ave.	Sept. 18	Turbid	528	.004	.060	.64	.035	35.0	87.0
1181	Fourth and I streets	Sept. 26	Clear	300	.420	.104	1.86	.045	6.0	94.0
1200	"	Oct. 9	Turbid	458	.152	.168	2.56	.045	8.0	89.0
1229	"	Oct. 16	"	412	.164	.240	3.80	.015	8.0	111.0
1182	10th, between B and C	Oct. 30	very turbid	300	.008	.032	1.36	.005	58.0	59.0
1389	5th and D streets	Oct. 9	Turbid	1094	..	.164	.92	.035	25.0	467.5
1434	E, between 8th and 9th	Dec. 12	sl. turbid	300	.004	.060	.62	.015	15.0	51.0
		Dec. 31	Cloudy							
2249	575 17th street	1889.	Turbid	620	.008	.140	1.16	.048	55.0	102.5
		July 29								
3184	12th and E streets	1890.	Turbid	302	.060	.280	2.10	trace	25.0	22.5
	Average	June 10	..	509	.158	.170	.174	.077	24.1	114.6

Suspicious or Contaminated Wells.—Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Chlorine.
69 87	<i>Northwest Section.</i> G, between New Jersey ave. and N. Capitol 6th, between F and G	1887. Sept. 27 Oct. 3	Clear "	741 340	.095 .028	.065 .060	.62 .40	30.0 23.0	143.8 58.8
730	" "	1888. May 29	"	374	.040	.144	.58	3.0	42.0
90 117 148 150 188	3rd, between L and K 6th and H streets 5th, between P and Q streets L, between 6th and 7th B and 2nd streets	1887. Oct. 3 Oct. 10 Oct. 17 Oct. 17 Oct. 24	" Turbid " " "	795 260 400 430 379	.040 2.280+ .022 .074 .032	.048 .440 .056 .044 .096	.50 7.46 .58 .98 .36	90.0 trace 25.0 24.0 16.0	190.0 77.5 75.0 106.0 78.6
354 554 644 765 789 489	1006 16th street F, between 1st and 2nd streets Louisiana ave. and 6th streets 8th, between G and H streets " " H, between 4th and 5th	1888. Jan. 16 April 3 April 28 June 12 June 19 Mar. 20	Turbid " Clear Turbid Cleaned "	965 884 840 464 446 224	3.520+ .020 .052 2.160+ 1.522+ 1.065+	.408+ .072 .188 .268 .132+ .332+	5.36 1.42 .82 3.40 3.04 3.46	.2 58.0 45.0 10.0 13.0 25.0	672.5 232.0 181.0 95.8 103.8 25.5
764	" "	1888. June 5	Clear	684	.140	.064	.88	35.0	158.5

Suspicious or Contaminated Wells. Northwest Section, Continued.

Serial No.	LOCALITY.	Date.	Condition.	Color.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrate.	Nitrogen as Nitrate.	Chlorine.
817	K, between 4th and 5th . . .	June 19	Turbid	..	1058	.332	.120	3.18	.070	45.0	199.8
979	4th and M streets . . .	Aug. 7	Turbid	..	520	.060	.108	1.12	.000	15.0	99.8
998	" . . .	Aug. 14	Cloudy	..	506	.000	.060	.84	trace	25.0	90.3
1024	D, bet. 1st and 2nd, cleaned .	Aug. 21	Turbid	..	270	.320	.108	2.70	.035	6.0	39.8
1058	" . . .	Aug. 28	Milky	..	196	1.280	.148	2.10	.010	5.0	22.3
1119	" . . .	Sept. 18	Turbid	..	189	1.540+	.060	1.16	.015	trace	18.0
1097	12th and N streets . . .	Sept. 11	Clear	..	212	.060	.044	.36	.005	8.0	38.5
1099	8th and F streets . . .	Sept. 11	Turbid	..	384	.060	.096	1.30	.035	8.0	44.8
1100	I, between 1st and 2nd . . .	Sept. 11	"	..	160	1.760+	.280	7.38	.075	trace	18.8
1171	26th, between E and F . . .	Oct. 6	Clear	..	972	.008	.072	.70	.006	55.0	149.5
1199	Q, between 2nd and 3rd . . .	Oct. 16	Sl. turbid	..	204	.012	.048	.90	.015	25.0	42.5
1251	6th and K streets . . .	Nov. 6	Turbid	..	270	.024	.112	1.44	.025	66.0	66.0
1269	9th and I streets . . .	Nov. 13	Clear	Yellow tinge	291	.004	.048	.68	.045	15.0	57.5
1270	36th and O streets . . .	Nov. 13	"	Blue tinge	986	.004	.060	.66	.035	45.0	136.5
1339	Pierce and New Jersey ave. .	Dec. 4	Milky	..	286	.060	.132	3.52	.025	15.0	54.0
1387	L, bet. 6th and 7th streets . .	Dec. 12	Sl. turbid	Blue tinge	526	.000	.068	.50	.013	25.0	112.5
1432	23d and G streets . . .	Dec. 31	Turbid	Yellow	302	.048	.173	1.06	.025	18.0	74.0
1476	I, between 21st and 22d . . .	Jan. 14	tur. odor	Yellow tinge	450	.104	.244	.50	trace	13.0	94.5
1482	W. C. Orphans' Asylum . . .	Jan. 15	Turbid	Yellow	84	.060	.052	.10	.015	6	21.5
1732	L and New Jersey ave. . .	April 22	Sl. turbid	..	356	.032	.040	.16	.018	18.0	76.3
1858	N. J. ave., bet. 6th and 7th .	May 20	Milky	Yellow	520	.032	.100	.54	.030	28.0	119.5
1892	" . . .	May 28	Turbid	Slightly yellow	480	.020	.112	.68	.024	8.0	113.8
1893	Stoughton street . . .	May 28	Clear	Straw	72	.020	.232	2.46	.000	1.1	3.8
2079	441 M street . . .	June 25	"	..	840	.004	.148	.36	trace	13.0	182.0
2147	3d and R streets . . .	July 9	"	..	400	.004	.072	.34	.020	35.0	78.3

Suspicious or Contaminated Wells. Northwest Section, Continued.

Serial No.	LOCALITY.	Date.	Condition.	Color.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
		1888.									
2185	R., between N. J. ave. and 5th	July 16	Clear	..	410	.920	.012	.21	.272	8.0	76.8
2263	"	Aug. 5	"	..	486	.108	.180	.56	.300	8.0	82.5
2220	3d, between G and H . . .	July 22	Sl. turbid	..	554	.008	.216	1.48	.020	18.0	116.0
2247	3d, between G and Mass. ave.	July 29	Turbid	..	710	.252	.060	1.70	.008	9.0	115.5
2284	736 5th street	Aug. 13	Clear	Yellow	820	.369	.140	1.76	.900	38.0	212.5
2381	507 Rhode Island ave. . . .	Aug. 26	Very turb	Light straw	412	.300	.420	3.06	.000	trace	51.0
2399	1034 4th street	Sept. 2	Milky	..	372	2.620+	.060	1.28	1.000	3.0	51.5
2408	3d and Indian ave.	Sept. 9	Clear	..	406	trace	.240	.28	.032	25.0	74.0
2519	12th and O	Sept. 30	Turbid	..	332	6.560+	1.080+	8.30	.020	0.0	32.5
2534	5th and Ridge	Oct. 7	Clear	..	460	.040	.188	.50	.020	35.0	87.0
2536	3rd and Indiana ave	Oct. 7	"	..	392	.020	.152	.66	.024	15.0	72.5
2539	10th, between T and V . . .	Oct. 7	"	..	780	.228	.200	.90	.360	38.0	139.0
2570	23rd and New York ave. . .	Oct. 14	"	..	244	.304	.100	.44	.065	15.0	19.0
2596	8th, below G and H	Oct. 21	"	..	380	.620	.100	.78	.020	15.0	62.5
2724	N. Y. ave., bet. 17th and 18th	Nov. 25	"	..	566	.040	.184	2.30	.025	48.0	99.0
		1890.									
2886	"	Jan. 21	"132	.360	1.22	.004	27.0	93.5
2888	1419 New York avenue . . .	Jan. 21	"	4.080+	.520	4.60	.200	70.0	37.5
2896	N. J. ave., between L and M	Jan. 28	"	..	564	.400	.672	8.36	.075	15.0	137.5
2980	F, between 1st and 2nd . . .	Feb. 24	"	..	1270	.032	.120	.42	trace	48.0	24.50

Suspicious or Contaminated Wells. Northwest Section, Continued.

Serial No.	LOCALITY.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
2994	F, between 1st and 2nd	Mar. 11	Clear	. .	.012	.088	.36	.002	35.0	244.5
2981	Mississippi ave., between 1st and N. Capitol	Feb. 24	"	811	.012	.112	.42	.008	25.0	199.0
2993	"	Mar. 11	"	. .	.100	.128	.50	.005	28.0	189.5
3018	7th and H	Mar. 25	"	380	.212	.192	.42	.008	15.0	76.0
3077	"	April 22	"	336	.104	.104	.50	.005	15.0	74.5
3151	"	May 27	"008	. .	74.5
3258	"	July 15	"	442	.212	.072	. .	.240	. .	82.5
3471	"	Sept. 30	"	366	.192	.032	1.04	.110	6.0	74.5
3065	10th street	"	400	.228	.252	.82	.038	25.0	65.5
3202	6th, between F and G	June 17	"	504	.140	.112	.04	.115	25.0	74.5
3235	C, between 21st and 22nd	July 2	"	1294	.892	.412	3.64	.065	35.0	172.5
3256	"	July 15	"240	. .	133.0
3323	480 Louisiana ave.	Aug. 5	"	87	.192	.112	.70	.038	1.6	9.0
3324	215 E	Aug. 5	Chalyb	514	.100	.320	2.04	.000	trace	147.5
3335	G and North Capitol	Aug. 12	Clear	512	.132	.292	.48	.125	11.0	110.0
3354	"	Aug. 19	"	362	.292	.360	1.98	.045	6.0	79.0
3382	"	Aug. 26	"	402	.232	.684	2.90	.025	6.0	70.0
3379	Louisiana ave., between 9th and 10th	Aug. 26	Milky	148	.280	.280	3.56	.000	.0	11.2
3414	404 15th street	Sept. 9	Clear	159	.752	.500	2.16	.068	5.0	32.5
3457	O, between 31st and 32d	Sept. 23	"	131	.032	.280+	.22	trace	1.92	34.0
	Average	478	.489	.188	1.65	.067	23.8	92.7

Averages of Results for the Several Sections and Classes.

Section.	Class.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitric.	Nitrogen as Nitric.	Chlorine.	Number of Analyses.
Northwest,	Passable	274	.014	.079	.56	trace	12.4	44.0	28
	Suspicious or bad	478	.489	.188	1.65	.067	23.8	92.7	79
	All	423	.359	.159	1.35	.049	20.7	71.5	107
Southwest,	Passable	566	.008	.048	.88	.000	28.0	111.0	1
	Suspicious or bad	606	.230	.215	1.56	.040	20.7	123.7	38
	All	605	.224	.211	1.54	.041	23.3	123.3	39
Northeast,	Passable	262	.023	.083	1.03	trace	21.2	33.1	5
	Suspicious or bad	599	.158	.170	1.74	.077	24.1	114.6	17
	All	410	.126	.151	1.58	.059	19.1	96.1	22
Southeast,	Passable	261	.044	.099	.67	trace	10.4	52.4	20
	Suspicious or bad	568	.305	.224	1.52	.022	24.6	104.0	31
	All	443	.201	.175	1.19	.014	19.2	85.1	51
County,	Passable	118	.028	.086	.83	.001	3.2	16.0	16
	Suspicious or bad	191	.637	.287	2.08	.087	3.6	33.1	21
	All	158	.203	.199	1.54	.050	3.5	25.7	37
District,	Passable	237	.021	.086	.69	trace	9.2	41.6	70
	Suspicious or bad	486	.361	.209	1.67	.058	21.5	90.8	186
	All	415	.265	.175	1.39	.042	18.1	81.3	256

The classification, upon which the preceding averages are based, results in a striking contrast between the passable and the suspicious or bad waters; that is to say, waters in which nitrogen is present as nitrites in amount exceeding .005 parts per million average much higher than those having less than this amount, in solids, free and albuminoid ammonia, oxygen consumed and chlorine. When nitrites are present, therefore, they seem generally to be an indication of contamination and to coincide with the results revealed by other determinations, except, perhaps, in such a case as their persistence in deep well water, and here other evidences of contamination are generally absent. The introduction of the nitrifying ferment by roots of plants from the soil, as illustrated in a well to be mentioned further on, is at times the cause of the presence of much nitrogen as nitrites, accompanied by high ammonia and oxygen consumed where the pollution is not of a dangerous character, and the general presence of calcium carbonate in the waters, of course, contributes to the flourishing growth of this ferment when once introduced.

The presence of nitrogen as nitrites also shows without doubt an active or present state of pollution, since they are the transition form in the oxidation of ammonia to nitrates and in waters where this oxidation is complete or not in progress nitrites will disappear. On this ground it seems fair to regard a water containing nitrites as very suspicious, and to condemn it if the remaining determinations are unfavorable, but the contrary cannot be asserted as always true, for with high nitrates and chlorine, showing the presence of oxidized filth, it is impossible to say when the contamination may cease to be thoroughly oxidized and become dangerous.

On the grounds of this classification it seems, however, that averages have been obtained for this locality which ought to serve as good and trustworthy standards of local purity, and that we may accept the averages for the passable wells of the different sections as representing their present ground water uncontaminated by any immediate or active pollution and as showing the amount of oxidized filth derived from the contamination of the soil by its support of population for a period of years. How far this source of pollution has affected them is shown by comparing the results

for the City sections with that for the County, which being a thinly populated area, its waters may be regarded as comparatively free from the products of such pollution. These harmless oxidized products are thus seen to be quite large and are particularly well shown by the nitrogen present as nitrates, which, amounting to only an average of 3.2 parts per million in the County, reach from 10.4 to 21.2 parts in the City. The number of analyses in Southwest and Northeast sections are, however, too small for any reliable conclusion as to what an uncontaminated water in these sections would be. In no waters of the District should they, apparently, appear in more than the amount of 30 to 40 parts per million without their condemnation.

Chlorine, from the nature of the soil, is much higher in the Southwest section than elsewhere, but in all the sections, pollution, either present or past, is accompanied by an increase of this element, the 16 parts per million of the passable waters of the County being increased to 44.0, 33.1 and 52.4 parts in the passable waters of the City, and again these latter amounts doubled or more than doubled in the suspicious or bad waters of their particular sections. Chlorine thus appears, when considered in conjunction with the local standard, to be a striking evidence of the nature of the water except in the case of the several mineral springs supplying a few wells.

Similar increases over the amounts in the passable waters are also seen in the averages for the other determinations, free and albuminoid ammonia and oxygen consumed.

The value of the local standards is thus well established, and in interpreting any particular analysis of a shallow well in the District, the following considerations may rule and many of them apply elsewhere as well.

1. Nitrites should be absent, or, if present in small amount, should not be accompanied by chlorine in excess of the local standard, but their absence may point to present oxidation, or reduction, which, in the presence of other high determinations, may not continue.

2. More than .005 parts per million of nitrogen as nitrites generally points to active changes sufficiently large to mark the water at once as suspicious or condemn it in conjunction with

abnormal chlorine or other high determinations. Those nitrites derived from roots, when oxygen consumed and free ammonia are high, are not as dangerous as those accompanying sewage with high chlorine, and albuminoid ammonia quickly evolved.

3. When albuminoid ammonia and oxygen consumed are abnormal, even in the absence of nitrites accompanied by low or normal chlorine, the contamination is probably vegetable, at least in the wells of the District. Such waters are not dangerous, but may be sufficiently deleterious or unpleasant to reject them or necessitate cleaning and protection of the well. This form of contamination generally originates in rotten wood in the wells or from the surface, either in storm water or drippings from the pump, which flow into the well. It appears to carry the nitrifying germ with it less frequently than soil water contamination, and at times reduction of the nitrites and nitrates in the well takes place.

4. Abnormally high chlorine points to contamination of animal origin.

5. All these considerations must be viewed in the light of the environmental evidence, and frequently the chemical evidence is too doubtful to derive any definite opinion from it, thus throwing the whole weight upon the former, a state of affairs incomprehensible to the ordinary layman, but which should always be made understood. Great responsibility should never be thrown on the chemical analyses alone, except in cases of gross pollution or marked changes from a known condition, and it is rarely, if ever, safe to pronounce a shallow well good upon such ground, alone or upon a single analysis, as will appear later.

Of the wells analysed, but a little over twenty-seven (27) per cent. were even passable, and of these many might be well placed in the suspicious class.

Of the latter class, many have been abandoned and filled, but the majority, not absolutely dangerously polluted, have been left in use because the environmental evidence failed to condemn, and because in parts of the city the aqueduct supply is inadequate, and in addition its temperature in summer, often reaching 88° F., makes it unpalatable and the cool water very desirable for the poor who cannot purchase ice.

ANALYSES OF PARTICULAR WELLS AND SPRINGS AT INTERVALS OF TIME.

With the object of studying the changes in the water of particular wells and springs at different seasons of the year, and before and after heavy precipitation, several were selected and examined at intervals of a month. These were picked out early in the course of the investigation, before any definite knowledge of their character was known, with the hope that they would prove typical, and included both good and bad waters, and illustrate the varying nature of the soil water. As will be seen from the following results, all but one or two of the wells were seriously contaminated and so much affected by local conditions that an independent view of the nature of the ground water is not obtained in any of the wells, and but partly so in the spring.

ANALYSES OF WELLS AT INTERVALS.

Well, Tenth and K Streets, Northwest.

Serial No.	Date.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.	Precipitation in Previous Week.
	1887.									
153	Oct. 18	Clear	310	.004	.040	.26	none	20.0	55.5	. .
285	Dec. 20	"	370	.016	.080	.28	none	21.0	57.5	. .
	1888.									
356	Jan. 17	"	350	.028	.064	1.08	none	25.0	50.0	.79
419	Feb. 21	"	350	.024	.072	.88	.002	25.0	50.5	.10
486	Mar. 20	"	366	.012	.072	.90	trace	18.0	49.5	.01
590	April 17	"	336	.008	.072	.66	trace	18.0	47.0	.97
700	May 22	"	310	.008	.060	.22	trace	18.0	46.5	.47
814	June 19	"	360	.008	.032	.38	trace	18.0	52.3	.62
878	July 17	"	372	.032	.076	.28	trace	18.0	52.8	3.37
1019	Aug. 21	Slightly turbid	330	.008	.060	.64	trace	25.0	53.8	.67
1116	Sept. 18	Clear	368	.008	.060	.94	.035	20.0	54.8	3.79
1202	Oct. 16	"	415	.028	.048	.56	.005	28.0	46.3	.26
1297	Nov. 22	"	336	.008	.136	1.52	trace	23.0	52.5	2.18
1415	Dec. 17	"	406	.034	.056	.76	.015	18.0	57.0	2.89
	1889.									
1479	Jan. 14	"	363	.008	.120	.74	trace	12.0	53.0	.48
		Average . .	356	.016	.069	.67	.004	20.5	51.5	

Well on Wilson Street.

Serial No.	Date.	Weather.	Condition.	Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
301	1887. Dec. 27	. .	Clear	110	.012	.080	.80	.014	2.0	24.0
373	1888. Jan. 31	.63	"	. .	.072	.232	.30	.025	4.0	29.0
445	Feb. 28	1.20	"	165	.024	.032	.22	.025	3.0	21.2
520	Mar. 27	1.82	"	136	.032	.020	.24	.018	1.0	26.5
622	Apr. 24	.52	"	122	.060	.012	.34	.015	2.0	25.0
733	May 29	1.67	"	126	.008	.024	.18	.018	2.0	26.0
832	June 26	.69	"	124	.004	.036	.36	.005	5.0	26.8
910	July 24	.07	"	134	.008	.032	.20	trace	15.0	28.5
1055	Aug. 28	1.13	"	122	.008	.040	.28	trace	2.0	32.0
1140	Sept. 26	.10	"	124	.004	.008	.16	trace	3.0	29.5
1231	Oct. 30	1.93	"	120	.024	.020	.70	.000	6.0	27.5
1323	Nov. 27	.36	"	116	.012	.048	.48	.010	3.4	27.5
1424	Dec. 24	.30	"	. .	.020	.024	.64	.000	5.0	27.5
1510	Jan. 21	1.39	"	105	.020	.060	.26	.015	5.0	27.5
1588	Feb. 18	1.43	"	146	.024	.092	.26	.030	3.0	27.5
1656	Mar. 25	2.14	"	114	.008	.112	.30	.012	3.0	28.0
				126	.021	.055	.36	.012	4.4	27.1

Well at Twelfth and O Streets, Northwest.

Serial No.	Date.	Weather.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
288	1887. Dec. 20	. .	Clear*	. .	.036	.028	.46	.010	32.0	105.0
355	1888. Jan. 17	.79	"	450	.048	.068	.32	.035	35.0	94.0
420	Feb. 20	.10	"	515	.040	.060	.32	.045	30.0	94.5
583	Mar. 13	1.65	"	470	.108	.032	.40	.055	25.0	88.0
589	Apr. 10	.40	"	428	.060	.060	.46	.053	25.0	81.0
699	May 22	.47	"	386	.060	.064	.30	.030	28.0	72.3
813	June 19	.62	"	260	.012	.060	.08	.017	18.0	91.8
877	July 17	3.37	"	448	.020	.160	.36	trace	25.0	91.3
1021	Aug. 21	.07	"	437	.032	.108	.30	trace	18.0	98.8
1138	Sept. 26	.10	"	480	.060	.032	. .	.035	25.0	99.9
1201	Oct. 16	.26	"	348	.008	.100	.78	trace	25.0	92.5
1296	Nov. 20	2.18	"	414	.280	.148	1.12	.032	25.0	84.0
1413	Dec. 17	2.59	"	466	.076	.082	.48	.025	38.0	84.5
1478	1889. Jan. 14	.46	"	442	.064	.080	.36	.015	15.0	84.0
				396	.065	.077	.46	.025	26.0	90.1

* With blue tinge.

Well at Seventeenth and K Streets, Northwest.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	1887.									
46	Sept. 13	. .	Clear	317	.005	.030	.80	. .	15.0	49.0
267	Dec. 13	. .	"	255	.008	.028	.36	.020	24.0	59.5
	1888.									
343	Jan. 11	.31	"	255	.080	.080	.48	.050	20.0	47.0
401	Feb. 13	1.29	"	265	.144	.076	.64	.040	25.0	46.5
484	Mar. 20	.01	"	288	.172	.060	.58	.130	18.0	45.5
575	April 10	.40	"	285	.128	.040	.58	.130	18.0	47.5
670	May 15	1.74	"	252	.064	.076	.30	.060	15.0	43.0
786	June 12	.04	"	254	.072	.040	.38	.075	18.0	43.8
870	July 10	.48	"	242	.072	.032	.16	.125	25.0	39.7
995	Aug. 14	1.18	"	250	.060	.032	.36	.050	18.0	46.0
1102	Sept. 11	2.62	"	232	.100	.032	.28	.125	18.0	43.0
1177	Oct. 9	.32	"	250	.060	.032	.52	.015	25.0	42.5
1265	Nov. 13	.38	"	248	.060	.052	.68	.025	15.0	46.0
	1889.									
1459	Jan. 7	1.52	"	218	.060	.096	.68	.018	13.0	43.5
1542	Feb. 11	.26	"	236	.100	.060	.50	.025	12.0	44.5
1614	Mar. 11	.10	"	288	.140	.173	.74	.026	15.0	44.5
1675	Apr. 9	2.27	"	308	.020	.048	.50	.018	18.0	44.5
Average				261	.079	.058	.50	.058	18.3	45.6

Well on North Capitol street between B and C Streets.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	1887.									
262	Dec. 5	. .	Clear	120	.020	.080	.90	.001	5.	27.5
302	Dec. 27	. .	"	175	.004	.064	1.54	.064	5.6	19.5
	1888.									
364	Jan. 24	.26	"	180	.358	.112	3.44	.080	4.0	19.5
446	Feb. 28	1.20	"	190	.164	.060	1.40	.140	5.0	17.5
519	Mar. 27	1.82	"	184	.220	.060	1.28	.380	2.9	19.0
621	Apr. 24	.52	"	185	.212	.072	1.08	.056	6.0	19.5
732	May 29	1.67	"	184	.136	.060	.84	.004	3.0	22.3
833	June 26	.69	"	190	.064	.076	.50	.068	8.0	21.8
911	July 24	.07	"	208	.064	.024	.44	.125	6.0	24.8
1056	Aug. 28	1.13	Clear, blue tinge	172	.044	.012	.32	.015	8.0	27.3
1139	Sept. 26	.10	"	166	.040	.020	.34	.025	8.0	24.5
1232	Oct. 30	1.93	"	110	.216	.080	1.48	.018	6.0	17.5
1325	Nov. 27	.36	Light, turbid, yellow	126	.140	.176	.90	.035	6.0	19.5
	1889.									
1425	Dec. 24	.30	Clear, blue tinge	. .	.200	.068	1.50	.015	6.0	19.0
1509	Jan. 21	1.39	Clear, yellow tinge	170	.500	.100	.70	.015	5.0	19.0
1590	Feb. 18	1.43	Clear	162	.100	.140	.78	.015	8.0	19.5
1655	Mar. 25	2.14	"	164	.112	.148	.50	.015	5.0	23.5
Average				152	.152	.1080	1.06	.063	5.7	21.3

Well on Seventh Street, one-fourth mile out.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
126	1887. Oct. 10	. .	Clear	370	.088	.136	.68	.003	14.0	111.0
372	1888. Jan. 31	.63	"	. .	.012	.056	1.84	.015	30.0	162.5
444	Feb. 28	1.20	"	590	.000	.224	.90	.006	58.0	127.0
518	Mar. 27	1.82	"	520	.036	.120	1.60	.058	35.0	110.0
620	April 24	.52	"	499	.008	.192	1.02	.035	25.0	108.5
731	May 29	1.67	"	504	.200	.192	1.44	.008	26.0	124.8
831	June 26	.69	"	502	.008	.132	.82	.015	25.0	110.8
909	July 24	.07	"	456	.032	.176	1.38	.015	18.0	97.8
1054	Aug. 28	1.13	Clear, blue tinge	474	.020	.240	1.22	.015	5.0	108.8
1137	Sept. 26	.10	Turbid, yellow	272	.148	.192	2.12	.015	15.0	110.5
1230	Oct. 30	1.93	"	304	.200	.360	3.80	.000	9.0	56.0
1324	Nov. 27	.36	"	284	.360	.172	1.84	.005	13.0	59.5
1423	Dec. 24	.30	"	. .	.392	.148	3.82	trace	15.0	57.5
1511	1889. Jan. 21	1.39	Clear	262	.500	.300	1.96	.005	8.0	48.5
1589	Feb. 18	1.43	Milky	258	.668	.400	2.38	.002	5.0	47.5
1657	Mar. 25	2.14	Turbid, yellow	308	.680	.505	4.88	.035	8.0	44.5
1698	April 15	.30	Slightly turbid	306	.160	.240	2.34	.005	15.0	38.0
Average . . .				348	.207	.223	2.00	.014	18.4	89.6

Well at Fifth and I Streets.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
92	1887. Oct. 3	. .	Clear	480	.024	.080	1.36	.020	30.0	111.0
287	Dec. 20	. .	"	. .	.020	.088	2.24	.050	12.0	95.0
344	1888. Jan. 10	.31	"	405	.040	.108	2.34	.025	10.0	92.5
402	Feb. 14	1.29	"	420	.012	.144	1.82	.050	10.0	91.0
485	Mar. 20	.10	"	440	.020	.072	1.88	.025	10.0	94.5
576	April 10	.40	"	420	.060	.100	.72	.028	15.0	96.0
661	May 8	.17	"	446	.032	.072	1.78	.050	15.0	98.5
672	May 15	1.74	"	474	.012	.120	1.60	.050	8.0	100.5
788	June 12	.04	"	394	.008	.108	1.50	.068	15.0	109.3
867	July 10	.48	"	520	.032	.104	1.32	.015	25.0	113.0
994	Aug. 14	1.18	Cloudy	490	.100	.048	1.32	.075	8.0	97.0
1101	Sept. 11	2.62	Clear	422	.576	.048	1.54	.390	18.0	91.0
1179	Oct. 9	.32	"	428	.828	.040	1.30	.015	15.0	91.0
1268	Nov. 13	.38	Slightly turbid	418	1.360	.300	6.44	.075	8.0	89.0
1388	Dec. 12	.06	"	442	.332	.060	.64	.275	12.0	87.5
1449	1889. Jan. 7	1.52	Clear	442	.912	.252	2.18	.175	15.0	89.0
1543	Feb. 11	.26	Turbid	414	1.320	.200	3.56	.190	15.0	87.5
1728	April 22	.87	Slightly turbid	426	1.460	.108	2.38	.035	15.0	93.8
2216	July 2	2.68	Slight odor; yellow turb.	416	1.480	.092	1.12	.192	8.0	94.8
Average . . .				439	.454	.113	1.95	.095	13.8	95.9

Well at Maryland avenue and Four-and-a-half Street.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	1887.									
185	Oct. 24	. .	Turbid	545	.040	.136	.56	.002	20.0	148.0
261	Dec. 2024	.092	.78	.002	25.0	161.5
	1888.									
318	Jan. 3	.85	Clear	580	.056	.108	1.46	.200	20.0	183.5
389	Feb. 7	.74		610	.072	.060	.74	.075	35.0	157.0
468	Mar. 6	.44	"	700	.200	.040	1.18	.325	25.0	166.0
552	April 3	.62	"	600	.080	.032	.48	.140	48.0	189.0
649	April 28	.00	"	578	.116	.104	.24	.032	18.0	182.5
762	June 5	.90	"	600	.060	.032	.30	2.000	25.0	174.5
851	July 3	2.00	"	604	.040	.076	.36	.045	25.0	155.0
965	July 31	.53	"	462	.000	.060	.32	.038	15.0	150.5
1074	Sept. 4	.29	"	466	.076	.032	.78	.035	15.0	132.5
1163	Oct. 2	.10	"	435	.100	.060	.50	.025	28.0	137.5
1255	Nov. 6	trace	"	448	.240	.040	.88	.075	25.0	139.5
1342	Dec. 4	.05	"	552	.800	.072	.76	.075	15.0	196.0
1429	Dec. 31	.32	"	514	.060	.140	.50	.035	15.0	154.0
	1889.									
1533	Feb. 4	.09	"	532	.104	.120	.44	.038	18.0	160.5
1665	April 2	.43	"	544	.472	.288	.76	.175	18.0	169.5
Average . . .				548	.149	.088	.65	.195	23.0	162.2

Well on Tenth Street, between N and O, Northwest.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
	1887.									
286	Dec. 20	. .	Clear	275	.720	.132	3.00	.375	11.0	53.0
	1888.									
357	Jan. 17	.79	"	240	.088	.056	.56	.045	6.0	49.5
487	Mar. 13	1.65	"	240	.184	.300	2.28	.090	28.0	42.5
591	April 10	.40	"	242	.060	.032	.80	.075	28.0	46.0
698	May 22	.47	"	274	.060	.072	.46	.013	15.0	49.8
815	June 19	.62	Turbid	124	.008	.120	3.02	.000	4.0	6.8
879	July 17	3.37	"	178	.008	.216	3.78	.000	.6	3.8
1020	Aug. 21	.67	Turbid, yellow tinge	132	.008	.084	5.98	trace	5.0	6.3
1117	Sept. 18	3.79	"	143	.012	.108	2.00	trace	15.0	6.7
1298	Nov. 22	2.18	"	128	.008	.152	2.06	.000	trace	4.5
1414	Dec. 17	2.59	"	132	.006	.100	1.50	trace	6.0	4.5
	1889.									
1477	Jan. 14	.46	"	176	.004	.292	2.30	.028	1.2	4.5
Average 1st period				254	.222	.118	1.42	.120	17.6	48.1
Average 2nd period				145	.008	.154	2.95	.004	4.5	5.3

* Cleaned.

Sixth and Massachusetts Avenue, Northwest.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
91	1887. Oct. 3	. .	Turbid, yellow	500	.022	.018	.54	.000	13.0	170.0
833	1888. June 26	.69	"	907	.332	.036	1.24	.240	18.0	248.0
970	Aug. 7	.31	"	932	.322	.064	.92	.000	3.0	268.8
1023	Aug. 21	.67	Clear, yellow	792	.184	.060	.84	.048	15.0	238.0
			Average . . .	783	.215	.045	.89	.077	12.3	231.2

Averages Compared.

LOCALITY.	Total Solid.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
10th and K st., northwest .	256	.016	.069	.67	.004	20.5	51.5
Wilson street	126	.021	.055	.36	.012	4.4	27.1
12th and O sts., northwest .	396	.065	.077	.46	.025	26.0	90.1
17th and K sts., northwest .	261	.079	.058	.50	.058	18.3	45.6
N. Capitol, bet. B and C sts. .	152	.152	.080	1.06	.063	5.7	81.3
7th st. road, ¼ mile out . .	348	.207	.223	2.00	.014	18.4	29.6
5th and I sts., northwest . .	439	.454	.113	1.95	.095	13.8	95.9
Maryland av. & 4½ sts., s.w.	548	.149	.088	.65	.195	23.0	162.2
10th st., bet. N & O, n.w., 1st	254	.222	.118	1.42	.120	17.6	48.1
10th st., bet. N & O, n.w., 2d	145	.008	.154	2.95	.004	4.5	5.3
6th and Mass. av., n.w. . . .	783	.215	.045	.89	.077	12.3	231.2

None of these waters is absolutely above suspicion, as they all contain nitrogen as nitrites, but there are great differences between them, which are instructive. The water in the wells at Tenth and K streets, Northwest, was, with four exceptions, but traces of nitrites or none, and from most of these analyses an opinion would be formed that the water was passable. This shows, that from any single analysis it is not entirely safe to form a definite decision as to the character of a water, as in this case it would result in passing the well on August 21st and putting it in the suspicious class on September 18th. The change must be brought about by varying conditions affecting some of the sources of supply.

Chief among these in this instance must be precipitation, which exercises a variable leaching effect upon the soil ; but our analyses are hardly frequent enough to follow this. The changes are within such limits and of such a nature as to show that the contamination is not of a dangerous character, but are, nevertheless, large enough to show what may be expected, even in a passable city well. The water from Wilson street would pass on five occasions out of sixteen, but the eleven other samples show so much nitrogen as nitrites as to make it probable that this water was subjected to some source of pollution of a variable nature. The well is one outside the city limits, in a thinly populated region, and from the low figures for nitrates and chlorine and their slight changes, evidently is not subjected to sewage contamination. The solids, too, are small in amount, and the ammonia in both forms low, so that it seems reasonable to view the presence of nitrites with less than the usual alarm, especially as the environmental evidence shows that there is nothing in the surroundings to cause contamination. Nevertheless, from the standpoint of the chemist, it would not do to pass this well as unsuspecting, owing to the presence of the nitrifying germ in an active state. The water in the well at Twelfth and O streets illustrates still more strongly the changeable nature of the shallow city wells. With its high solids varying much in amount, its high nitrates and chlorine, the almost constant pressure of variable but large amounts of nitrites, and the lack of satisfactory environmental evidence, condemns this well without a doubt, but as the amounts of albuminoid ammonia is not excessive, it is probable that there is a slow and irregular oxidation going on of a small amount of filth, gradually reaching the well in one irregular way and varying with precipitation and other causes.

Of the well at Seventeenth and K streets, everything in regard to the preceding well can be repeated, but the extremely high figures for nitrogen as nitrites on many occasions point to a much greater amount of nitrification at present going on in this water than in that at Twelfth street, and yet this well is, and has been for years, in constant use by a very large number of persons without the slightest ill effect being observed. The chemical evidence in this case was not considered sufficient to close the well, and it

is still in use. The constancy and low amount of the chlorine, the small amount of oxygen consumed, and of albuminoid ammonia, shows that nitrification and oxidation take care, at present, of the pollution coming to this water, but the well remains suspicious because it cannot be told when the pollution will become so great as to be absolutely dangerous and not completely oxidized. The water in the well at North Capitol street is of quite a different character from all the preceding ones. It is the first to show high amounts of free ammonia and oxygen consumed combined with very variable nitrites and at the same time low nitrates and chlorine. We have here the first undoubted evidence of primary contamination, that is to say, with non-oxidized organic matter. The absence of an amount of chlorine, large for that section, and the very low nitrates, shows that the pollution is vegetable organic matter and comparatively innocuous. It is extremely variable, and due probably to surface storm water, and perhaps some roots of trees. The well on the Seventh street road was found to be taking much storm water from a heavily traveled unpaved road and from its own drippings. Removing these sources of contamination in October immediately improved the water, an improvement which increased as the well gradually cleaned itself, but in the meantime much free and albuminoid ammonia were present. The great variations in the nitrates in this well, greater than in any of the preceding, seems to point to their destruction from time to time and renewal. The high chlorine also shows in this section that much of the pollution must have been of animal origin.

At Fifth and I streets a typical and interesting well was found. When first examined, the water was suspicious, but not filthy, but toward the end of the summer of 1888, the roots of the rapidly growing shade trees in its neighborhood had reached the water in such a mass as to produce from August to November a rise in free ammonia of from .100 to 1.360 parts per million, and to introduce the nitric ferment in large amount. This was unaccompanied by changes in the amount of chlorine, but was, of course, in that of oxygen consumed. All this is typical of this peculiar form of contamination.

In November the well was cleaned, and the December analysis

showed a corresponding improvement, but it was merely temporary, for the roots again took possession with the same result as before, and the well was abandoned. After cleaning, the nitrites were at their highest, showing a more favorable opportunity for nitrification than in the constant presence of excess of organic matter in the previous month, which evidently brought about reduction.

At Maryland avenue a well was examined which was classed as suspicious on the ground of the chemical evidence, but nothing could be found in the environmental evidence to condemn it, so it was stated. After many analyses, however, and continued adherence to the idea that some source of pollution must exist, a careful investigation showed that it was liable to pollution from two drain pipes. The greatest irregularities marked this water, the nitrogen as nitrites varying from .002 to 2.000 parts per million, and the chlorine and free ammonia in like manner, well illustrating the effect of sewage contamination.

The well at Tenth and O streets proved remarkable in that it changed its character in a marked degree in June, 1888. This I have attributed to a leak of aqueduct water into the well, as it has never been otherwise explained. At all times the water was so irregular in character as to show something wrong in its source of supply, and it was therefore condemned and abandoned, and the same was the case with the Sixth street well which follows.

All these analysis proved thus to be quite instructive, although not in the lines originally sought, and serve as good examples upon which to base interpretations of other analysis as well as to point out the danger of too hasty conclusions from simple examinations. In the light of these results, it has been found advisable where a well appears very suspicious to have it cleaned and then analysed again.

I may add that the wells which have been described, are probably as a whole as good or better than those of other large cities. Analyses of 110 wells in New Haven, classed in accordance with the suspicious nature of their surroundings, the most suspicious in the first class, and so on were made in 1886 by Drs. Smith and Lockwood. Their averages are as follows :

32 CHARACTERISTICS OF WELL AND SPRING WATERS.

Class.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
1	713	4.09	.15	.09	36	72
2	348	1.46	.12	.06	17	31
3	673	2.57	.12	.10	38	70
4	302	.20	.12	.11	11	25

As a whole these are bad waters and dangerous. Some individual analyses show passable wells, others water little better than sewage, as for example :

Well No. 15.

Total solids	1542
Free ammonia45
Albuminoid ammonia47
Nitrogen as nitrites15
Nitrogen as nitrates	87
Chlorine	185

Disease was plainly attributable to some of these wells, but similar rank pollution has never been equaled in the District, and, owing to the supervision of our wells, probably never will be. If the wells are to be kept open a liberal appropriation for their care and protection is indispensable ; or, what I should suggest as the safest policy would be that in those portions of the city where they are most in need and where it is possible a number of deep wells be sunk by boring and cased to the bottom with iron pipe so as not to admit of the possibility of surface contamination.

ANALYSES OF SPRING WATERS.

Monthly Analyses of Water from the Capitol Spring.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
232	1887. Nov. 15	. .	Clear	104	.040	.028	.18	trace	6.00	12.0
269	Dec. 13	. .	"	. .	.008	.008	.14	.000	2.00	8.0
316	1888. Jan. 3	.85	"	305	.034	.040	.20	.000	4.00	7.5
390	Feb. 7	.74	"	80	.032	.080	.10	.005	3.00	8.5
466	Mar. 6	.44	"	72	.008	.072	.38	.000	3.00	7.0
550	April 3	.62	"	58	.008	.072	.30	.000	.30	6.0
647	April 28	.00	"	90	.032	.060	.34	.000	2.50	8.5
760	June 5	.90	"	80	.004	.052	.16	.000	.36	8.5
850	July 3	2.00	"	84	.016	.032	.20	.000	.36	9.5
967	Aug. 7	.31	"	59	.000	.000	.18	trace	2.40	9.5
1073	Sept. 4	.29	"	102	.032	.060	.20	.005	1.60	8.7
1162	Oct. 2	.10	"	60	.004	.020	.16	.003	3.00	7.0
1253	Nov. 6	trace	"	80	.008	.032	.46	trace	3.00	7.5
1341	Dec. 4	.05	"	66	.020	.052	.16	.000	2.50	7.0
1430	1889. Jan. 1	.32	"	42	.004	.048	.16	trace	2.80	7.5
1532	Feb. 4	.09	"	54	.024	.104	.16	.000	2.80	6.5
1594	Mar. 15	.04	"	42	.012	.140	.24	.000	1.80	7.5
1667	April 2	.43	"	68	.012	.060	.16	.000	2.50	8.0
Average . . .				85	.017	.053	.21	.000	2.40	8.0

Franklin Square Spring.

Serial No.	Date.	Precipitation in Previous Week	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrites.	Nitrogen as Nitrates.	Chlorine.
268	1887. Dec. 13	. .	Clear	268	.008	.020	.18	.000	20.0	47.0
342	1888. Jan. 10	.31	"	305	.028	.120	.18	trace	20.0	55.0
403	Feb. 13	1.29	"	330	.032	.060	.18	trace	25.0	53.5
481	Mar. 13	1.65	"	320	.012	.072	.24	.000	18.0	55.5
574	April 10	.40	"	324	.000	.032	.28	.000	20.0	54.5
659	May 8	.17	"	350	.040	.064	.34	.000	18.0	54.5
671	May 15	1.74	"	346	.008	.060	.08	.000	25.0	55.5
787	June 12	.04	"	304	.004	.032	.28	trace	16.0	54.0
871	July 10	.48	"	. .	.008	.060	.16	.000	30.0	53.7
996	Aug. 14	1.18	"	340	.000	.032	.44	.000	15.0	50.8
1103	Sept. 11	2.62	"	322	.004	.008	.22	.008	15.0	53.8
1178	Oct. 9	.32	"	350	.060	.032	.16	trace	1.5	52.5
1267	Nov. 13	.38	"	304	.004	.032	.48	.000	13.6	51.5
1390	Dec. 12	.06	"	290	.000	.012	.18	trace	.8	57.5
1447	1889. Jan. 7	1.52	"	328	.000	.076	. .	trace	5.8	57.5
1541	Feb. 11	.26	"	296	.000	.060	.22	trace	11.2	56.0
1616	Mar. 11	.10	"	284	.012	.100	.24	.000	5.5	54.5
1674	Apr. 9	2.27	"	302	.004	.072	.48	trace	25.0	56.0
Average				315	.012	.050	.24	trace	10.8	54.1

34 CHARACTERISTICS OF WELL AND SPRING WATERS.

City Spring C Street and Sixth Street and Pennsylvania Avenue.

Serial No.	Date.	Precipitation in Previous Week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrate.	Nitrogen as Nitrate.	Chlorine.
201	1887. Nov. 1	. .	Clear	356	.044	.048	.36	trace	22.0	66.0
276	Dec. 18	. .	"	250	.028	.056	.26	trace	10.0	46.0
317	1888. Jan. 3	.85	"	370	.032	.132	.30	.000	18.0	61.5
388	Feb. 7	.74	"	355	.008	.128	.28	.005	18.0	59.5
467	Mar. 6	.44	"	335	.004	.060	.24	.000	15.0	60.0
551	April 3	.62	"	355	.008	.072	.36	trace	17.0	61.5
648	April 28	.00	"	348	.012	.072	.42	.000	15.0	62.5
761	June 5	.90	"	364	.000	.060	.18	.000	9.0	65.3
849	July 3	2.00	"	394	.008	.068	.24	.000	11.0	66.0
966	Aug. 7	.31	"	330	.000	.024	.30	trace	9.0	75.2
1073	Sept. 4	.29	"	400	.040	.028	.30	.018	.6	63.0
1161	Oct. 2	.10	"	340	.008	.032	.32	trace	11.6	60.0
1254	Nov. 6	trace	"	358	.012	.092	.52	.000	11.0	59.5
1340	Dec. 4	.05	"	296	.008	.084	.22	.000	5.6	64.5
1428	1889. Jan. 1	.32	"	324	.004	.108	.30	trace	18.0	58.0
1531	Feb. 4	.09	"	306	.000	.092	.30	.000	15.0	59.0
1593	Mar. 15	.04	"	364	.252	.192	.96	trace	13.0	63.0
1668	April 2	.43	"	324	.004	.088	.36	.000	15.0	60.5
Average . . .				343	.026	.080	.34	trace	13.0	61.7

P Street Spring.

Serial No.	Date.	Precipitation previous week.	Condition.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrate.	Nitrogen as Nitrate.	Chlorine.
934	1888. July 31	.53	Cloudy	198	.048	.108	1.52	.038	9.0	37.3
1104	Sept. 11	2.62	Sl. cloudy	188	.032	.132	.78	.025	11.6	28.8
1180	Oct. 9	.32	Cloudy	168	.012	.032	.56	trace	9.0	29.0
1266	Nov. 13	.38	Sl. cloudy	170	.024	.120	.86	trace	7.0	33.0
1391	Dec. 12	.06	Cloudy	184	.008	.080	.56	.032	6.5	27.5
1448	1889. Jan. 7	1.52	"	200	.008	.240	2.56	.005	5.5	27.5
1540	Feb. 11	.26	"	162	.000	.136	.36	.012	5.6	27.5
1617	Mar. 11	.10	"	164	.004	.172	.44	trace	6.0	25.6
1673	Apr. 9	2.27	Sl. cloudy	166	.004	.112	.22	.013	15.0	27.0
Average				178	.016	.126	.87	.015	8.3	29.2

The average results for each of these springs are here compared :

Springs.	Total Solids.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.	Nitrogen as Nitrates.	Nitrogen as Nitrates.	Chlorine.
Capitol spring	85	.017	.053	.21	.000	2.4	8.0
Franklin Square spring . .	315	.012	.052	.24	trace	10.8	54.1
City spring	343	.026	.080	.34	trace	13.0	61.7
P street spring	178	.016	.126	.87	.015	8.3	29.2
Deep Well, Country, 130 ft.	174	.000	.020	.22	.000	0.0	4.0

The Capitol spring is situated without the city limits, in the bed of what has become the new reservoir, near the Soldiers' Home, and has been, I believe, properly protected during the recent excavations. It should not, from its situation, be liable to any pollution. The water is conveyed to the Capitol.

The Franklin Square spring is in the center of Franklin Square, and is well removed from immediate sources of pollution. The water is conveyed in numerous directions, and supplies many hydrants on the streets and several buildings.

The City spring is situated on C street, beneath the building on the north side, between Four-and-a-half and Sixth, now occupied by C. J. Bell as a photolithographic establishment. It is ceiled up under the flooring, and the water is conveyed by pipes to many neighboring stables and hotels, and to a hydrant on the southwest corner of Sixth and Pennsylvania avenue. Its flow is large. It is liable at any time to serious contamination from a soil-pipe from an adjacent water closet.

The P street spring is found on P street, in a gravel bank, just off the sidewalk, between Twenty-second and Twenty-third streets, on the north side. It is protected by a brick vault, but is liable to contamination from surface drainage.

For comparison, the analysis of a deep well in the Columbia gravels on the highest river terrace is given, since it is so much like the spring waters.

All these waters showed a striking contrast to the well waters. That from the P street spring is alone contaminated, and the source there is surface drainage and improper protection. The

remaining springs differ only that the two within the City limits carry a much larger proportion of solids than the Capitol spring, but from their large flow from considerable depths seem to take up but small portions of contamination of the products of oxidized filth from the surface soil or neighboring pollution. The character of these waters is probably that of the best of this region before its settlement.

WASHINGTON, D. C.,
November, 1890.

THE UNIT FOR ATOMIC WEIGHTS.

By W. A. Noyes.

Of the recent determinations of the atomic weight of oxygen, only one has given a higher value than 15.90. Lord Rayleigh* has found the ratio of the densities of hydrogen and oxygen to be 1 : 15.884. Morley† has recently determined the ratio of the combining volumes of the two gases with very great accuracy, and finds the value 1 : 2.00023. Morley‡ has also determined the ratio of the densities, and finds 1 : 15.884. Cooke§ has found the value 1 : 15.882, making use of the density of oxygen as found by Regnault and corrected by Crafts. From the values 1 : 15.884 and 1 : 2.00023 we have 15.882 as the atomic weight of oxygen. Van der Plaats|| thought that he had obtained values from 15.94 to 15.96 for the atomic weight in question, by burning measured volumes of hydrogen. He undoubtedly used, however, the old value for the weight of a liter of hydrogen, and when his results are calculated with the value obtained by Morley and by Rayleigh, the atomic weight is 15.86 to 15.88. Cooke and Richards** have found the value 15.869 by burning weighed quantities of hydrogen. Lord Rayleigh†† has found the value 15.89 by the combination of weighed amounts of oxygen and hydrogen. I have found‡‡ the value 15.896. Keiser,§§ alone, has found the higher value 15.949.

*Proc. Roy. Soc. 43, 356.

†In a paper read before the American Association for the Advancement of Science, August, 1890. See also, Nature 42, 530.

‡Ibid.

§Am. Chem. Jour. 11, 509.

||Am. Chim. Phys. 1886, 7, 529.

**Am. Chem. Jour. 10, 191.

††Proc. Roy. Soc. 43, 425.

‡‡Am. Chem. Jour. 11, 441.

§§Am. Chem. Jour. 10, 249.

I have elsewhere pointed out a source of error which, I think, accounts for at least a part of the difference between this value and that obtained by all other recent workers in this field.

Morley* has also recently pointed out a probable source of error in Dumas' determinations.

It would seem to be almost certain, therefore, that the true value cannot be greater than 15.90. Personally, I believe future determinations will show that the true value lies between 15.88 and 15.90. In any case, we are no longer justified in using the value 15.96.

If chemists generally accept this conclusion, the question of what unit we shall use for the atomic weights will acquire a new significance. We must either adhere strictly to the hydrogen unit and recalculate all other atomic weights, or we must make oxygen our practical standard, as has been suggested by Venable, Brauner, and others, giving to it the value of 16. Some of the reasons for advocating the latter course have been very well stated in a recent number of this Journal by Professor Venable. There is one point, however, which it does not seem to me was made sufficiently clear. Very many of the atomic weights approximate so closely to whole numbers, when we place $O=16$, that the nearest whole number can be used for all ordinary calculations. Meyer and Seubert have objected to this point that chemists can still use whole numbers for calculations, whatever values are given in accurate tables of atomic weights. This is, of course, true, but it is certainly very undesirable to have $Pb=205.5$ ($O=15.89$) in our tables of atomic weights and then use $Pb=207$ for calculations. Of course the use of the nearest whole number, $Pb=206$, would be, in such a case, entirely unjustifiable.

That the point urged is an important one, will be apparent, I think, from the following table. I have used the table given by Meyer and Seubert as the basis of this table because they are the chief opponents of the use of $O=16$ as a standard, and because their table must be conceded to be free from any bias in favor of whole numbers. Recent determinations have given us more accurate values for a number of the elements, and the table cannot be considered as representing our present knowledge of atomic weights.

*Am. Chem. Jour. 12, 460.

O = 16.			O = 15.89.		
	Difference.	Per cent.		Difference.	Per cent.
H = 1.007	+ 0.007	0.7	H = 1	—	—
Li = 7.03	+ 0.03	0.43	Li = 6.98	— 0.02	0.29
B = 10.93	— 0.07	0.64	B = 10.86	— 0.14	1.28
C = 12.00	—	—	C = 11.92	— 0.08	0.67
N = 14.04	+ 0.04	0.28	N = 13.94	— 0.06	0.43
O = 16.00	—	—	O = 15.89	— 0.11	0.69
F = 19.11	+ 0.11	0.58	F = 18.98	— 0.02	0.11
Na = 23.05	+ 0.05	0.22	Na = 22.89	— 0.11	0.48
Mg = 24.00	—	—	Mg = 23.84	— 0.16	0.67
Al = 27.11	+ 0.11	0.41	Al = 26.92	— 0.08	0.30
Si = 28.07	+ 0.07	0.25	Si = 27.88	— 0.12	0.43
P = 31.05	+ 0.04	0.13	P = 30.83	— 0.17	0.55
S = 32.06	+ 0.06	0.19	S = 31.84	— 0.16	0.50
Cl = 35.46	— 0.04	0.11	Cl = 35.22	— 0.28	0.79
K = 39.13	+ 0.13	0.33	K = 38.86	— 0.14	0.36
Ca = 40.01	+ 0.01	0.03	Ca = 39.74	— 0.26	0.65
Cr = 52.58	+ 0.08	0.15	Cr = 52.22	— 0.28	0.54
Mn = 54.93	— 0.07	0.13	Mn = 54.55	— 0.45	0.82
Fe = 56.02	+ 0.02	0.04	Fe = 55.64	— 0.36	0.64
Ni = 58.74	— 0.26	0.44	Ni = 58.33	— 0.67	1.15
Co = 58.75	— 0.25	0.42	Co = 58.34	— 0.66	1.13
Cu = 63.34	+ 0.34	0.54	Cu = 62.91	— 0.09	0.14
Zn = 65.04	+ 0.04	0.06	Zn = 64.59	— 0.41	0.63
As = 75.1	+ 0.10	0.13	As = 74.58	— 0.42	0.56
Bi = 79.96	— 0.04	0.05	Bi = 79.41	— 0.59	0.74
Sr = 87.52	+ 0.02	0.02	Sr = 86.92	— 0.58	0.67
Ag = 107.93	— 0.07	0.06	Ag = 107.19	— 0.81	0.76
Cd = 111.98	— 0.02	0.02	Cd = 111.22	— 0.78	0.70
Sn = 117.64	— 0.36	0.30	Sn = 116.94	— 1.06	0.91
Sb = 119.9	— 0.10	0.08	Sb = 119.1	— 0.90	0.75
I = 126.86	— 0.14	0.10	I = 125.99	— 1.01	0.80
Ba = 137.2	+ 0.20	0.15	Ba = 136.3	— 0.70	0.51
Pt = 194.78	— 0.22	0.12	Pt = 193.44	— 1.56	0.81
Au = 196.69	— 0.31	0.16	Au = 195.34	— 1.66	0.85
Hg = 200.3	+ 0.30	0.15	Hg = 198.9	— 1.10	0.55
Tl = 204.2	+ 0.20	0.10	Tl = 202.8	— 1.20	0.59
Pb = 206.91	— 0.09	0.04	Pb = 205.49	— 1.51	0.74
Bi = 208	—	—	Bi = 206.6	— 1.40	0.68
Ur = 240.4	+ 0.40	0.17	Ur = 238.8	— 1.20	0.50
Mean	0.11		Mean	0.55	

A careful examination of the differences given in the second column for O=16 shows that for only six elements (Na, S, K,

Ag, I, and Pt) are these differences greater than the possible inaccuracies of the atomic weights as estimated by Meyer and Seubert.* For three of these (Ag, I, and Pt) the differences are only 0.06 and 0.12 per cent. of the atomic weights. I do not mean to imply by this that the atomic weights are not in most cases a little greater or smaller than the nearest whole number. But it is evident that when careful determinations of an atomic weight have not established with *certainty* that it is greater or less than the nearest whole number, that nearest whole number is sufficiently accurate for use in calculating the results of ordinary analyses.

It will only rarely be necessary to use the value 1.007 for hydrogen if we make $O=16$ the basis for our atomic weights. The only common compounds containing hydrogen are salts containing water of crystallization, ammonium compounds, and organic compounds. In a salt containing 30 per cent. of water, it makes a difference of only 0.02 per cent., whether we calculate the composition with $H=1$ or with $H=1.007$.

In analysing organic compounds, the hydrogen is always weighed in the form of water, and if we calculate one-ninth of the weight of the water as hydrogen, the error arising from this assumption almost exactly compensates for the error in calculating the amount of hydrogen in the compound by the use of $H=1$. For the other elements in organic compounds, the error is usually small, and very seldom reaches 0.05 per cent.

ROSE POLYTECHNIC INSTITUTE,
January 3, 1891.

THE DETECTION AND ESTIMATION OF TITANIUM.

BY W. A. NOYES.

The methods commonly in use for the decomposition of minerals containing titanium are not very satisfactory. Fusion with potassium or sodium pyrosulphate is tedious, and the decomposition is frequently very incomplete. Solution in a mixture of hydrofluoric and sulphuric acids is sometimes easily effected, but it must be followed by evaporation to remove the hydrofluoric acid, and subsequent dilution rarely gives a clear solution. These difficulties have led me to seek for some modification which would give

*Die Atomgewichte der Elemente, p. 242.

better results. The following method I find to work well in the cases to which it has been applied :

For a quantitative determination by Weller's method,* take 0.1 gm. of the finely powdered mineral and mix it in a platinum crucible with 0.2 gm. of sodium fluoride, also finely powdered. Add 3 gms. of sodium pyrosulphate without mixing. Then fuse carefully, holding the burner in the hand. Heat gently till the effervescence ceases and copious fumes of sulphuric acid are evolved. This takes only two or three minutes. When cold, the mass in the crucible is dissolved in 15 to 20 cc. of cold water and the solution filtered. The filtrate and washings need not exceed 30 cc. If a residue remains, it can be treated again by the same method, after burning the filter, but the amount of titanium found by a second fusion is usually very small.

To the solution, 1 cc. of hydrogen peroxide and a few cc. of dilute sulphuric acid are added, and the color obtained is compared with that of solutions containing known amounts of titanium. For a standard solution, titanous oxide is dissolved in hot concentrated sulphuric acid and the solution diluted till 1 cc. contains 1 mg. of TiO_2 . In diluting, it is best to use dilute sulphuric acid at first to prevent the precipitation of titanous oxide.

I cannot entirely confirm Weller's statement that the colors produced are not affected by small amounts of iron. I find that even 2 mg. of ferric oxide in the form of sulphate has a very decided effect on the tints produced, especially when the amount of titanium is small. It is advisable, therefore, to add to the comparison tubes an amount of ferric sulphate corresponding approximately to that in the solution which is tested. A solution of iron ammonium alum answers well for this purpose, and all that is necessary is to match the color of the solution of the mineral before adding hydrogen peroxide to it. If this is done, titanium can be readily determined in the presence of very considerable amounts of iron. Thus, 0.02 mg. of titanous oxide can be detected in 30 cc. of water in the presence of 0.1 gm. of ferric oxide in the form of sulphate. This would correspond to 0.02 per cent. for 0.1 gm. of a mineral.

A qualitative test for titanium can be made in five minutes, as

*Ber. d. chem. Ges. 15, 2592.

follows: Mix a little of the powdered ore with sodium fluoride, add sodium pyrosulphate, and fuse as above. Cool by dipping the crucible in cold water. Add 2 or 3 cc. of dilute sulphuric acid and 10 cc. of water. Dissolve by boiling. Divide the solution in two portions, and to one add a few drops of hydrogen peroxide. A comparison with the solution to which no hydrogen peroxide has been added will show at once whether titanium is present or not.

It seems possible that by the method of decomposition described some of the titanium might volatilize as titanium fluoride. To determine whether an appreciable error would arise from this source, 0.1 gm. of titanite oxide was fused with sodium fluoride and sodium pyrosulphate. When cold, the fused mass was dissolved in water and the solution made up to 100 cc. 1 cc. of the solution in 30 cc. of water gave the same tint with hydrogen peroxide as 1 cc. of the standard solution. Determinations based on a comparison of tints cannot be made very accurate, but they are especially valuable for the determination of small quantities of elements, and for most cases where titanium requires determination, the method which is given above is amply accurate.

The method which is here given works excellently with magnetite and with other iron ores.

ROSE POLYTECHNIC INSTITUTE,
January 3, 1891.

THE WELSBACH INCANDESCENT LIGHT.

BY EDWARD HART.

One of the most interesting incidents of the meeting of chemists at Philadelphia was the visit to the works of the Welsbach Incandescent Gas Light Co., at Gloucester, N. J. The principle of this lamp is that certain oxides, such as that of zirconium, when brought into the non-luminous flame of a Bunsen burner, become incandescent. The merit of the company consists in having succeeded in working out and applying in a commercial way this well-known fact.

The process begins with the weaving of an endless hollow cylinder of cotton thread. This is carried out with a knitting machine, the stitch being like that produced by a crochet needle. The end-

less bag is then carefully washed and dried, cut into lengths and saturated in the solution, which consists principally of a mixture of the nitrates of lanthanum yttrium and zirconium. It is then spread upon a spool which is rotated by machinery in a drying closet, so as to secure uniform distribution of the material. The cylinders are now each about 18 inches in length and are cut into two pieces of equal length and each piece gathered at one end by means of a platinum thread, Fig. 1. The ends of this thread, which project on opposite sides of the gather, are looped over an iron ring. The web cylinder is then spread over a former, so as to separate the threads and open the loops, and is then fired by bringing the flame of a Bunsen burner in contact with the top. The cotton ignites and burns off rapidly, leaving the oxides as a skeleton of the same form, but of course very much lighter (the ordinary size weighs 7 grains) and not so strong. This skeleton or mantle as it is now called is then condensed by ignition at a high temperature in the flame of a Bunsen burner and the ignition completed with a blast lamp. The bottom is now trimmed off evenly and is ready for the final operation, Fig. 4. In this condition the mantle is too frail for shipment, and to make it stronger it is dipped into a solution of kristaline (a celluloid preparation) and dried in an air bath. The mantles are packed in various ways, according to the size, but for the ordinary size in a pasteboard box, as shown in Fig. 5. *c* is the box, *a* the mantle fastened to the iron ring with wire standard, which slips into the loops *dd*, and *b* is a pasteboard cylinder which is fastened to the box-lid and projects into the mantle, holding it in place. Packed in this way the mantles are sent by mail, often making long journeys, and are very rarely broken. When received, they are put in position over a Bunsen burner and ignited. The kristaline burns off rapidly, and the lamp is ready for use. A completed burner in position is shown in Fig. 2. Fig. 3 shows a magnified section of the mantle photographed by its own light. A very careful study of the Bunsen burner has been made by the company, and has resulted in a number of improvements in the forms now used, which are models of simplicity and elegance. The advantages claimed for this light are that with the same amount of gas much more light is obtained, and second that it can be used with natural gas or fuel gas which do not give satisfactory results when burned in the ordinary way.

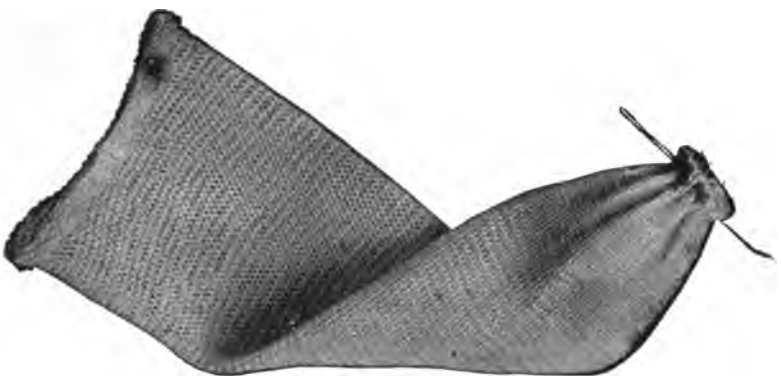


FIG. 1.

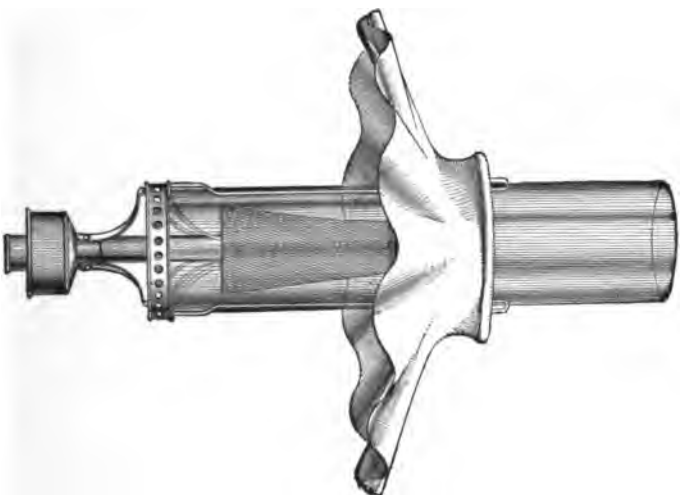


FIG. 2.



FIG. 3.

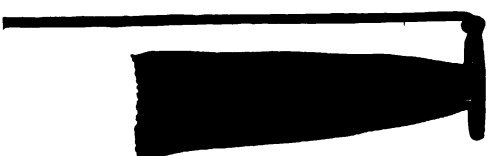


FIG. 4.

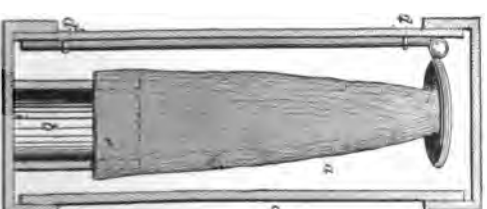


FIG. 5

The demand for this light is large and increasing. At the time of our visit, the works were turning out 8000 per week. The retail price of the light shown is \$2.50, and the mantels are supplied for 50 cents each, guaranteed to last for 500 hours.

In addition to the manufacture of their lamps, the company had on exhibition a magnificent collection of rare minerals and the salts derived from them. The display was enough to make a chemist's eyes water. It consisted of

150	kilos	lanthanum	and	ammonium	nitrate.
100	"	neodymium	"	"	"
10	"	praseodymium	"	"	"
10	"	yttrium	oxalate	from	fergusonite.
10	"	"	"	"	gadolinite.
50	"	zirconium	nitrate.		

Specimens of salts of erbium, yttrium, thorium and cerium; oxides, carbonates, sulphates, nitrates, chlorides, acetates, oxalates of neodymium and praseodymium; cerite, monazite, samarskite, allanite, zircons.

TREATMENT OF CUPRIFEROUS PYRITES AT HUELVA, SPAIN.

BY L. DE LAUNAY.

Annales des Mines has in Vol. XVI, pp. 427-516, a very elaborate and interesting article on the copper industry of the Huelva district, Spain. This essay, of which Mr. L. de Launay is the author, has been condensed in the following manner by *Proc. Inst. Civil Eng.*, CI, 374.

The author, after describing the geology and structure of the great pyrites mines of San Domingos, Tharsis, Rio Tinto, and others, proceeds to consider the methods adopted for exhausting the copper. These are classified as follows:

1. Natural cementation.
2. Artificial cementation.
3. Artificial cementation with chlorides.

The first of these methods, which is essentially one of atmospheric oxidation, is practised at San Domingos in Portugal, where the burning of pyrites in open heaps is forbidden by law. The ore, a cupriferous iron pyrites containing from 2.5 to 3.0 per cent.

of copper, is broken into lumps of the size of the fist and spread out on floors in heaps varying from 15 to 40 feet in thickness. Deep trenches are cut through the heap at regular intervals for the escape of drainage water, and a series of holes lined with earthenware pipes are sunk into it at the top for the purpose of inserting thermometers when it is desired to ascertain the temperature in the interior. Water is distributed over the surface by a rectangular network of pipes with jets, and the operation is continued for several years, about 3,000,000 tons being under treatment at one time. The sulphates formed by the joint action of air and water dissolve in the latter, and are collected in channels leading to the cementation tanks. The surface of the heap is broken up by a pick from time to time to prevent the crust of sulphates from becoming compact and impermeable to water. The operation, though extremely simple in principle, requires somewhat delicate management, especially in regard to temperature. If the heap is too cold, the sulphide of copper is not attacked, while if too hot, an excessive production of steam prevents the access of air and the consequent oxidation of copper, while a larger proportion of iron is dissolved. The best results are obtained at 100° F., a heat that is maintained by varying the amount of water. It is also essential that the solution shall be as rich in copper sulphate as possible, and if the liquors are too poor the watering of the heap is sometimes suspended from 15 days to a month.

When the proportion of copper in the heap is reduced from 2.8 to 0.25 per cent., the heap is broken up and exported for use as a sulphur ore, the process having the advantage of saving the bulk of the sulphur. The quantity of water required being very large, two storage reservoirs have been built for holding it, one being of 5,000,000 and the other of 1,500,000 tons capacity, the latter also serving for irrigation and domestic supply.

The liquors obtained from watering the heaps are led into the cementation tanks, which are asphalted basins 13 feet square, arranged in 10 series of 24. These are filled with pig iron piled chequerwise, and the coppery liquors are run through them in such a manner as to obtain the most complete precipitation with a minimum consumption of pig iron. The precipitated copper or

casara deposits on the surface of the pigs and is cleaned off at intervals of a month. The deposit, consisting of a mixture of copper with graphite and iron rust, containing about 65 per cent. of copper, is dried upon a heated surface and packed in bags of 100 pounds for export.

The consumption of pig iron, which theoretically should be only 0.83, is actually 2.0 per unit of copper obtained. This is due to the formation of ferric sulphate in the liquors, which must first be reduced to ferrous sulphate by the iron before any copper can be separated.

The exhausted liquor, essentially a ferrous sulphate solution, is stored in tanks, which, to avoid permanent poisoning of the river, are only emptied during the period of the spring floods.

Artificial Cementation.—This term is applied by the author to the method of burning the pyrites in heaps as a preliminary to extraction by water and precipitation, which is in general use in Spain, although at present attempts are being made to abolish it on account of the damage done by the sulphur gases. At Lagunazo, near Tharsis, where the ore contains from 2 to 3 per cent. of copper, with about 3 per cent. of arsenic, 2.3 ounces of silver, and about $1\frac{1}{2}$ pennyweight of gold per ton, it is burned in heaps called *teleras*, in a similar manner to that subsequently described as in use at Rio Tinto, for about two months.

The solution of the copper is effected in two stages, it having been found that ferric sulphate liquors will remove from one-eighth to one-fifth of the copper in the first ten days. The burnt ore is subjected to a first washing in tanks for twelve hours, followed by a second of twenty-four hours, and a third of forty-eight hours, after which it is piled into heaps called *terreros*, where the residual copper is extracted by watering, an operation which, like that in the natural cementation process, lasts for several years. The cementation is effected in tanks, through which a very rapid current is maintained, the iron being turned out every ten days; the amount of iron consumed is 1.7 per unit of copper obtained. The *casara* when dried and roasted in a reverberatory furnace, an operation which requires about 4 per cent. of its weight of coal, is packed in bags for export.

The deposit at Lagunazo was only opened in 1882. It now

produces about 120,000 tons of pyrites annually. About 1,000 tons of copper are obtained from 86,000 tons of burnt ore under treatment.

Artificial Cementation with Chlorides.—In this method, which is practised at Rio Tinto, the copper is dissolved, not as sulphate, but as chloride. This has the advantage of reducing the waste of iron in the precipitation tanks, by avoiding the formation of ferrous and ferric sulphates, as the solution of the sulphide of copper is effected by means of ferric chloride, while iron pyrites is but slightly acted on. By this means a ton of copper precipitate may be obtained with an expenditure of an equal weight of pig iron.

The produce of the mine is divided into five different classes, each having its own method of treatment. These are :

1. Smalls, obtained by sifting the larger sizes. These are subjected to a modification of Doetsch's process of washing by ferric chloride, as they pack too close to be converted to sulphates by atmospheric oxidation.

2. Ordinary ores with less than 2.75 per cent. of copper. These are burnt, watered, lixiviated, and precipitated.

3. Ores of 3.75 and 4 per cent. average, obtained when necessary by the mixture of other kinds. These are sent by rail to the pier at Huelva and shipped, those of 3.75 per cent. going to England, and those of 4 per cent. to Germany.

4. Rich ores above 6 per cent. These are unfit for calcination, and are, therefore, smelted for regulus in water-jacket cupolas.

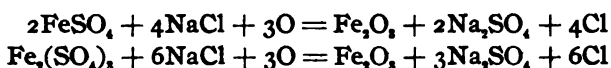
5. Minerals containing copper and lead. These are put aside as giving trouble in the ordinary working, and have not as yet been utilized.

Treatment of the Smalls by the Modified Doetsch Process.—This, which like the method of natural cementation at San Domingos, does away with roasting, but reduces the loss of time and iron by adding salt, is applied in practice with the following modifications :

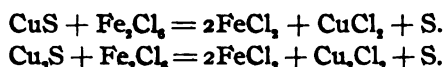
On the side of a hill below the *teleras*, or roasting heaps, there are five series of tanks, each series consisting of seven tanks 15 meters long, 4 meters wide, and $1\frac{1}{4}$ meters deep, which are divided into eight compartments by walls of perforated bricks, placed edgewise and covered by planks. At a lower level is placed another series of four larger tanks, 100 meters long, 2 meters broad,

and $1\frac{1}{4}$ meters deep. The whole are used indifferently for the treatment of the smalls, and for the first washing of the burnt ores, which extracts about one-fifth of their contents of copper, before sending them to the *terrerros* at Naya: The raw smalls are mixed with a proportion of burnt ore in lumps of the size of a walnut, and washed with liquors brought from the large *terrerros* containing a certain quantity of common salt. This operation lasts about eight days, the wash-water going to the precipitation tanks, while the partially exhausted mineral is taken to the *terrerros* at Naga. The reactions in this method appear to be as follows :

The burnt ore having been subjected, at a high temperature, to the action of oxygen and chloride of sodium, gives rise to :



The chlorine liberated, acting upon the sulphides of iron and copper, produces ferric and cupric chlorides. There are, therefore, present FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CuSO_4 , Fe_2Cl_6 , and CuCl_2 , with an excess of salt which changes the ferric sulphate into chloride. The copper in the ore existing partly as cuprous sulphide Cu_2S , and partly as cupric sulphide CuS , the reactions become :



the ferric chloride attacking and dissolving the copper, while the iron pyrites is almost untouched. The final separation of the copper is effected by cementation in the manner previously described.

Treatment of Ores with less than 2.75 per cent. of Copper.—This, the method of artificial cementation of chlorides, is applied to the largest part of the output of the mine. It includes the four operations of roasting, washing, precipitation, and cleaning of the precipitate, or *cascara*.

The roasting is performed in *teleras*, which are heaps of a truncated pyramidal form, three meters high, on a base of six by eight meters for those of 800 tons, and nine by eight meters when containing 1,200 tons. At the bottom, one transverse and three longitudinal flues, about 20 inches square, are formed by the

larger blocks of mineral. These are the firing passages, and communicate with vertical chimneys, of which there are two in the 800 ton and three in the 1,200 ton heaps. The mass of the heap is made up of lumps a little above nut size, salt being added in the proportion of 14 tons to 800 tons of pyrites. When the fire has been started with a little wood, it is kept up by the heat of the burning sulphur. It is essential that no rich ore shall be included, as, on account of the action of "kernel roasting," lumps of rich sulphide of copper are formed, which cannot be subsequently dissolved; and as the mass of material is so large that hand-picking is not easy, great loss of copper is likely to ensue. It need scarcely be said that the operation causes an enormous nuisance, as, since the introduction of the use of salt, the volatile products contain chlorine as well as sulphurous acid, and, especially during the prevalence of easterly winds, the village of Rio Tinto is almost uninhabitable from the sulphur smoke, while all vegetation is destroyed to a distance of six leagues around. This is now sought to be mitigated by removing the roasting heaps to a greater distance—at Planes, where large lead chambers are under construction for the purpose of saving from the sulphur gases the sulphuric acid required for cleaning the copper precipitate, and which has hitherto been purchased abroad. A more important application has, however, been found in using sulphurous acid gas for promoting the formation of sulphates in the ore, which is now carried out on a very extensive scale at Naya.

In this method, the *teleras* made in the ordinary way, as soon as they begin to give off sulphurous acid, are covered up with a fresh quantity of mineral, partly raw and partly calcined, to which 2 or 3 per cent. of salt and a similar proportion of peroxide of manganese have been added. The whole is formed into a heap 8 inches high with a flat top, which is divided by gutters into squares of 8 meters in the side. The remaining operations are effected in the usual way, the *teleras* being watered at intervals for months and years, the copper being slowly dissolved, and collected at the bottom of the heap. It is necessary to break up the surface with a pick at intervals, to prevent its becoming impermeable to water.

The sulphurous acid gas in this modification of the process, in

the presence of steam formed by the heat developed in the heap, produces sulphuric acid, which acts upon the oxides in the crust of the roasted mineral. The salt and manganese ore may, jointly with the sulphuric acid, evolve chlorine, forming ferric chloride, which decomposes the sulphides of copper and silver. It is also possible that, under the action of heat and sulphuric acid, oxygen is evolved, which acts directly upon the pyrites.

The precipitation of the copper is effected at La Cerda, near Rio Tinto, in a series of tanks 100 meters long and 30 meters broad, divided into 10 parallel series, receiving a uniform supply. The total length is about 400 meters, with a difference of level of four meters, giving a sufficiently rapid flow. Pig iron as run from the furnace and scrap are used, the latter being put into baskets. Every ten days the iron is removed, and after scraping to collect the deposited copper is returned to the tanks. The consumption is reduced to a little more than one ton of pig iron per ton of precipitate produced.

The *cascara* precipitate as collected is very impure, containing only 65 to 70 per cent. of copper, the remainder being ferric oxide, more or less arsenical, graphite from the pig iron, silica, etc. After treatment with water acidulated with sulphuric acid, which dissolves the basic ferric arseniates without touching the copper, it is passed over sieves of four-tenth inch mesh to separate any adherent masses of cast iron, which are hand-picked, and any copper separated is subjected to another washing with acid. The *cascara* passing through the sieves is washed in a current of water where it separates, according to the density, into *cascara*, or copper; *grafita*, or particles of coal and graphite; and *pucha*, a fine black sand. The *cascara* is subjected to a fresh washing upon a fine wire-gauze screen, which separates a further quantity of graphite, and this passes to a series of plunger jigging machines, where it is finally cleaned. The graphite is collected and returned to the rich ore smelting furnaces.

The *pucha* is washed upon convex round buddles 15 feet in diameter, by which a certain quantity of fine copper is saved. The waste is made into balls, which are dried in heaps and also sent to the smelting furnaces.

The silver in the pyrites usually remains in the *terreros*, a small proportion only passing into the copper precipitate.

The rich ores containing more than 4 per cent. of copper are, after burning, smelted in cupolas or water jacket furnaces of an American pattern, having a large exterior fore-hearth or receiver in which the separation of slag and regulus takes place. The charge consists of burnt ores, old slags, a certain proportion of raw pyrites, quartz and graphite. The regulus, which is exported to England, contains from 38 to 40 per cent. of copper; the slags with 0.4 per cent. are thrown away.—*Eng. and Min. Journal.*

RESOLUTIONS ADOPTED AT A CONFERENCE OF CHEMISTS ASSEMBLED FOR CONSIDERING THE FORMATION OF A NATIONAL ORGANIZATION,

HELD DECEMBER 30TH AND 31ST, 1890, AT THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

About eighteen delegates from the following Chemical Societies were present, to wit:

1. American Association for the Advancement of Science, Chemical Section; 2. American Chemical Society; 3. Franklin Institute, Chemical Section; 4. Brooklyn Institute, Chemical Section; 5. Association of Official Agricultural Chemists; 6. Chemical Society of Washington; 7. Manufacturing Chemists' Association, of the United States.

Prof. A. B. Prescott in the chair.

Resolution 1.—It is desirable that an American Association of Chemists be formed to embrace all existing American chemical organizations.

Resolution 2.—*Resolved*, That this Conference recommend to all existing American chemical organizations that they call a meeting of their bodies to be held in Washington in connection with the meeting of the American Association for the Advancement of Science for 1891, and that each of these organizations be requested to appoint a committee, or to continue their present committee for the further discussion of the subject submitted to the conference now in session.

Resolution 3.—*Resolved*, That this general conference committee, composed of the present sub-committees, or such others as may be appointed by the several organizations, be called together at as early a time as practicable before the joint meeting recommended in the resolution adopted.

Resolution 4.—Resolved, That meanwhile each sub-committee, through its chairman, shall formulate such modifications of the Constitution of the American Chemical Society as it shall deem necessary to adapt it to the requirements of the Association proposed.

Resolution 5.—Resolved, That the chairman of these sub-committees shall then, so far as possible, harmonize the views embodied in these reports of their several organizations, and shall have printed for presentation at the joint meeting a report, or majority and minority reports, on a Constitution for the proposed Association of American Chemists.

Voted, That the chairman of this conference, with Prof. Clarke and Prof. Hale, be a committee of three to select time and place for the meeting called for in Resolution No. 3.

Voted, to request the American Chemical Society to print the minutes of this conference in their Proceedings of the Philadelphia meeting, and to mail copies as widely as possible to Chemists in North America.

The Secretary of this Conference was desired to communicate the above resolutions to scientific journals, with a view to obtain a wide publication of the same.

Adjourned to meet at call of the chair.

H. CARRINGTON BOLTON,
Secretary.

COMMITTEE OF CONFERENCE, WITH SOCIETIES REPRESENTED.

Dr. A. C. Peale, U. S. Geological Survey, Washington, D. C.
Representing the Chemical Society of Washington.

Prof. F. W. Clarke, U. S. Geological Survey, Washington, D. C.
Representing the American Association for the Advancement of Science.

Dr. H. W. Wiley, Department of Agriculture, Washington, D. C.
Representing the Official Agricultural Chemical Association.

Mr. H. Pemberton, Jr., 29th & Gray's Ferry Road, Philadelphia, Pa.
Representing the Chemical Section of the Franklin Institute.

Mr. Henry Bower, 29th & Gray's Ferry Road, Philadelphia, Pa.
Representing the Mfg. Chemists' Association of the U. S.

Dr. Walter H. Kent, 64 Livingston St., Brooklyn, N. Y.
Representing the Brooklyn Institute.

Dr. E. Waller, School of Mines, Columbia College, New York City.
Representing the American Chemical Society.

SPECIFIC GRAVITY OF NITRIC ACID.

G. B. Squires, Ph. G., in a thesis presented to the Massachusetts College of Pharmacy, gave the results of his determinations of nitric acid in solutions varying from 1 to 50 per cent. strength of acid. There are two tables of nitric acid specific gravities more or less in use at the present time, one by Dr. Ure, and the other by J. B. Kolb, the former being the older, and nearly superseded by the latter. Dr. Ure's method of constructing his table was to obtain a pure acid of specific gravity 1.5, and then mix it in numbered vials with pure water in the proportion of 95 parts acid and 5 parts water, 90 parts acid and 10 parts water, 85 parts acid and 15 parts water, and so on for each variation of 5 per cent. Then taking the specific gravity of these liquids, he produced the framework for his table, claiming that the series of numbers thus obtained constituted a regular progression by which intermediate specific gravities could be stated.

Kolb's table embraces specific gravities at two temperatures 0° and 15° C. He took the gravities of several different dilutions, and afterwards transferred the liquid to a larger flask, making up to a definite quantity with water, and the percentage was obtained by neutralizing this liquid of known weight with dry and pure calcium carbonate, the excess of which was subsequently separated, dried and weighed. From these factors by calculation was obtained the percentage of anhydrous nitric acid.

The writer of this thesis, however, adopted a different procedure. Two pounds of sodium bicarbonate were packed firmly in a percolator and washed with an equal weight of water to remove any chlorides and sulphates it might contain. By this washing it lost about 15 per cent. in weight. It was then transferred to a drying rack where it remained until it became air dried. Four hundred and fifty gms. of this air dried salt were heated in a clean iron kettle until reduced to a carbonate, and from this salt was prepared 2,000 gms. of solution of soda U. S. P., which solution was very carefully standardized by an accurate solution of oxalic acid. With this standard soda solution was very carefully estimated, the percentage strength of the many solutions of nitric acid whose specific gravities were afterward obtained. The following table gives the specific gravities for each percentage of nitric acid from 1 to 50:

Per cent. Acid.	Sp. Gr. 15° C.	Per cent. Acid.	Sp. Gr. 15° C.
1	1.00581	26	1.15869
2	1.01136	27	1.16660
3	1.01713	28	1.17371
4	1.02286	29	1.18073
5	1.02851	30	1.18830
6	1.03439	31	1.19552
7	1.04019	32	1.20276
8	1.04592	33	1.20635
9	1.05234	34	1.21300
10	1.05746	35	1.22013
11	1.06330	36	1.22675
12	1.06951	37	1.23347
13	1.07581	38	1.23980
14	1.08126	39	1.24510
15	1.08843	40	1.25235
16	1.09500	41	1.25850
17	1.10102	42	1.26475
18	1.10725	43	1.27125
19	1.11321	44	1.27785
20	1.12024	45	1.28450
21	1.12714	46	1.29110
22	1.13349	47	1.29780
23	1.13890	48	1.30443
24	1.14460	49	1.31101
25	1.15164	50	1.31722

It was the author's intention to carry the work still further, but the task was found too great for the time at his disposal. The results have been thoroughly verified by estimates in duplicate and may be accepted as accurate.—*Pharm. Era*, Jan. 1, 1891.

THE DETERMINATION OF SULPHUR IN COPPER.

10 gms. of the sample is dissolved in pure 16*E** nitric acid (=sp. gr. 1.42), evaporated to dryness on the water bath, when the residue is taken up with 400 cc. of *E* nitric acid, filtered, if necessary, and any residue is reserved. The filtrate is diluted to 800 cc., heated to 70 C., 1 cc. of 5*E* HCl is added, and the solution is well stirred, and allowed to stand in the cold for twelve hours. The supernatant liquid is decanted as far as possible from the precipitate of silver chloride, which is finally filtered and washed, and the silver determined, if required, as customary. The filtrate is now evaporated almost to dryness. 50 cc. of 10*E* HCl (= sp. gr. 1.16) are

*See this Journal 4, 317.

added, when the solution is evaporated to dryness. The residue is dissolved in a small quantity of water, 50 cc. of 10*E* HCl are again added, and the solution again evaporated to dryness. The residue is now dissolved in 300 cc. of *E* HCl, diluted to 700 cc., heated to boiling, and 2 cc. of *E* barium chloride solution are added, the solution is stirred, and allowed to stand for twenty-four hours. The barium sulphate is then filtered off, ignited and weighed. The reserved residue, insoluble in nitric acid, is tested for sulphur, and if any is found, it is added to the original amount. (H. J. Phillips, Chem. News 62, 239. A. H. W.

CIRCULAR ON ATOMIC WEIGHTS.

By request of the Committee of Revision and Publication of the Pharmacopœia of the United States of America, Prof. F. W. Clarke, Chief Chemist of the U. S. Geological Survey, has furnished a Table of Atomic Weights, revised upon the basis of the most recent data, and his latest computations. The Committee has resolved that this table be printed and furnished for publication to the professional press. The Committee also requests that all calculations and analytical data which are to be given in reports or contributions intended for its use or cognisance, be based upon the values in the table. It would be highly desirable that this table be adopted and uniformly followed by chemists in general, at least for practical purposes, until it is superseded by a revised edition. It would only be necessary for any author of a paper, etc., to state that his analytical figures are based upon "Prof. Clarke's Table of Atomic Weights, of Dec. 6th, 1890," or some subsequent issue.

CHARLES RICE,

Chairman of the Committee of Revision, etc.

NEW YORK, December 20, 1890.

TABLE OF ATOMIC WEIGHTS.

(Issued December 6, 1890)

Revised for the Committee of Revision and Publication of the Pharmacopœia of the United States of America

BY F. W. CLARKE, Chief Chemist of the United States Geological Survey.

This table represents the latest and most trustworthy results, reduced to a uniform basis of comparison, with Oxygen = 16 as starting point of the system. No decimal places representing

large uncertainties are used. When values vary, with equal probability on both sides, so far as our present knowledge goes, as in the case of cadmium (111.8 and 112.2), the mean value is given in the table.

The names of elements occurring in pharmacopœia, medicinal, chemicals, are printed in heavy-faced type.

NAME.	Symbol	Atomic Weight.	NAME.	Symbol	Atomic Weight.
Aluminum . . .	Al	27.	Molybdenum .	Mo	96.
Antimony . . .	Sb	120.	Nickel	Ni	58.7
Arsenic	As	75.	Nitrogen . . .	N	14.03
Barium	Ba	137.	Osmium	Os	191.7
Bismuth	Bi	208.9	Oxygen § . . .	O	16.
Boron	B	11.	Palladium . . .	Pd	106.6
Bromine	Br	79.95	Phosphorus .	P	31.
Cadmium	Cd	112.	Platinum . . .	Pt	195.
Caesium	Cs	132.9	Potassium . .	K	39.11
Calcium	Ca	40.	Rhodium . . .	Rh	103.5
Carbon	C	12.	Rubidium . . .	Rb	85.5
Cerium	Ce	140.2	Ruthenium . .	Ru	101.6
Chlorine	Cl	35.45	Samarium . . .	Sm	150.
Chromium . . .	Cr	52.1	Scandium . . .	Sc	44.
Cobalt	Co	59.	Selenium . . .	Se	79.
Columbium* . .	Cb	94.	Silicon	Si	28.4
Copper	Cu	63.4	Silver	Ag	107.92
Didymium† . .	Di	142.3	Sodium	Na	23.05
Erbium	Er	166.3	Strontium . . .	Sr.	87.
Fluorine	F	19.	Sulphur	S.	32.06
Gallium	Ga	69.	Tantalum . . .	Ta	182.6
Germanium . . .	Ge	72.3	Tellurium . . .	Te	125.
Glucinum† . . .	Gl	9.	Terbium	Tb	159.5
Gold	Au	197.3	Thallium . . .	Tl	204.18
Hydrogen . . .	H	1.007	Thorium	Th	232.6
Indium	In	113.7	Tin	Sn	119.
Iodine	I	126.85	Titanium . . .	Ti	48.
Iridium	Ir	193.1	Tungsten . . .	W	184.
Iron	Fe	56.	Uranium	U	239.6
Lanthanum . . .	La	138.2	Vanadium . . .	V	51.4
Lead	Pb	206.95	Ytterbium . . .	Yb	173.
Lithium	Li	7.02	Yttrium	Yt	89.1
Magnesium . .	Mg	24.3	Zinc	Zn	65.3
Manganese . . .	Mn	55.	Zirconium . . .	Zr	90.6
Mercury	Hg	200.			

*Has priority over Niobium.

†Now split into Neo- and Praseo-Didymium.

‡Has priority over Beryllium.

§Standard, or basis of the system.

THE ANALYSIS OF IRON AND STEEL.

Determination of Phosphorus in Steel.—Dr. M. A. von Reiss, Stahl und Eisen, 1890, pp. 105-109. By this method phosphorus is determined by measuring the volume of the yellow precipitate. The following details are an improvement on those formerly published in Stahl und Eisen, 1889, p. 1025. 3.5 gms. of steel are dissolved in 50 cc. nitric acid, 1.23 sp. gr., and oxidized with permanganate, potassium oxalate being finally added. Add 80 cc. ammonium nitrate solution (160 gms. to 1 liter), and heat to boiling. Allow to come to 95 degrees, and precipitate with 50 cc. molybdate solution. The temperature, after addition of the molybdate, is about 75 degrees, and the yellow precipitate separates and settles quickly. The volume of the precipitate is not in direct proportion to the percentage of phosphorus, but by increase of the percentage of phosphorus, the volume increases at a slower rate, that is, the factor decreases regularly with increase of phosphorus. A table giving volumes and corresponding percentages is given.

Colorimetric Determination of Phosphorus.—Prof. Rud. Namias, Stahl und Eisen, 1890, p. 1060. The basis of the method is the intensely blue color which results when phosphomolybdate of ammonium is dissolved in a solution of sodium hyposulphite. A steel having a phosphorus content of about .05 per cent. is taken as a standard, and the phosphorus is accurately determined in it by a gravimetric method. The details of the colorimetric method are as follows: A sample of 1 gm. is dissolved in a small beaker in 10 cc. nitric acid of 24° B. After complete solution, 1 cc. hydrochloric acid is added, and the solution evaporated to dryness. The residue is dissolved by heating with 3 cc. HCl and 7 cc. HNO₃ of 24° B., and 50 cc. molybdate solution is added. Preliminary heating of the molybdate solution is recommended. Stir vigorously and set aside for one-and-a-half hours at a temperature of 50 degrees. The precipitate, including silica and graphite, is filtered off, and thoroughly washed with a warm 5 per cent. solution of ammonium chloride. The filter, with precipitate, is placed in a small beaker, and 30 cc. of a solution of 12 gms. sodium hyposulphite in 1 liter of water is added. The residues are heated, with occasional stirring, for one-half hour, to near 100 degrees in a water bath. The resulting blue solution is filtered

into the 50 cc. flask, the filter being washed with cold water until the filtrate reaches the mark. The filtrate is stirred, and is then ready for comparison with the standard steel. P. W. S.

VOLUMETRIC DETERMINATION OF MANGANESE.

The weighed quantity of manganese salt is dissolved in water, with 2 or 3 parts of potash-alum, and to the solution is added a measured quantity of a decinormal solution of iodine and pure soda-lye (free from nitrite). The whole is heated on the water-bath for from five to ten minutes, and diluted, when cold, to a given volume. An aliquot part is filtered off through a dry folded filter, the filtrate is acidulated, and the excess of iodine is titrated with solution of sodium thiosulphate, the number of cc. of the latter consumed is re-calculated from the total volume of the liquid and deducted from the quantity of iodine solution employed, and thus the quantity of solution of iodine required for oxidizing the manganoous oxide is determined. Manganese can be thus determined in presence of aluminum or iron salts, or in pig-iron, but salts of ammonium must not be present. (G. W. Vortmann, Chem. News 62, 251. Berichte 23, 2801.) A. H. W.

NOTES.

The Proposed New Chemical Society.—For many years a so-called American Chemical Society has been in existence. It has, however, never fully represented American chemists, and should have been called the New York Chemical Society. At the outset this society bid fair to draw into its membership all the American chemists; but two serious mistakes were made, which at once destroyed all chance of success. 1st, the meetings were limited to New York City. 2d, a black-list of delinquent members was published soon after the society was inaugurated. This last act of supreme folly immediately destroyed all hope of success, and the society has remained in a more or less moribund condition ever since. But for the self-sacrifice of a few devoted members, it would long since have died of inanition. At the Toronto meeting of the American Association for the Advancement of Science a committee was appointed to meet committees

from other organizations to consult with reference to the formation of a National Chemical Society. This committee reported progress, at Indianapolis, last summer, and was enlarged. Similar committees were appointed by The American Chemical Society, The Franklin Institute, The Association of Official Agricultural Chemists, The Washington Chemical Society, and The Association of Manufacturing Chemists of the United States. These various committees met at Philadelphia on December 30 and 31. The action taken there will be found reported in full in another part of this issue. In substance, they determined to meet again in Washington next year, and in the meantime try to come to a more definite agreement, so that the matter could then be finally settled.

That it is desirable to have an American Chemical Society all are agreed. As to what it shall undertake, there is a great difference of opinion. The greatest difference of opinion is manifested upon the point as to whether the new society should undertake to publish a journal, many who would probably be members, Dr. Prescott, Dr. Remsen, Dr. Bolton, Dr. Loeb, and others, holding that this can be done better by private enterprise, and that the publications of the new society should be limited to an account of the proceedings, and to an index of chemical papers.

The question, upon its merits is simply this: Can a journal be carried on best by an incorporated society or by individuals? We think when fairly looked at there can be no doubt as to the answer. While there are many excellent journals carried on by societies, as, for example, the *Journal of the Society of Chemical Industry* and the *Berichte der deutschen chemischen Gesellschaft*, they are all open to just criticism on three points. 1st. They soon grow to be large and unwieldy in size, and correspondingly expensive. The *Berichte* costs now 30 marks per annum, or about \$7.50. 2d. No one person alone is responsible for the contents, consequently a great deal of trash finds its way into print. All journals, no doubt, are more or less open to this criticism, but it is certainly true in the superlative degree of many society journals. 3d. Authors are compelled to publish their papers in the society journal, and generally lose the power to copyright the matter contained in them. Two chemical journals already exist in this country, one

of them devoted to pure chemistry and the other to analytical and applied chemistry. We think the ground is already well covered, and we know that no paper which can properly claim it will be refused publication in either journal. As at present conducted, those persons who are interested only in pure chemistry need only subscribe for *The American Chemical Journal*, and those who feel an interest only in analytical and applied chemistry, need subscribe only for *THE JOURNAL OF ANALYTICAL AND APPLIED CHEMISTRY*. We know of a very large number of cases where this practice is followed to advantage. If a new journal is established, those now in existence will surely lose support, and in all probability be extinguished. It has been proposed that a committee appointed by the new society assign the papers for publication to either of the two journals now in existence; a better plan is to leave this matter entirely in the hands of the author of the paper, a practice which has been followed to advantage for many years by the American Association for the Advancement of Science. By following this plan, the offices in the disposal of the new society would be unpaid, and the annual meeting would resolve itself into friendly contests for the honors to be bestowed, and not into desperate struggles for the flesh pots, led by rival cliques.

Azoimid N₂H.—In 1887 Curtius discovered that by warming triazoacetic acid with dilute sulphuric acid the sulphate of a new nitrogen compound, N₂H₄, or hydrazin, was formed.* By heating the solution of the salt with caustic potassa, the hydrate, N₂H₄H₂O, is formed, boiling at 119°. At the boiling temperature, this attacks glass and destroys cork and rubber. It is a strong reducing agent, and combines with aldehydes.

Curtius has now succeeded in making Azoimid N₂H.† This is prepared by the action of hydrazin-hydrate upon benzoylglycolic acid. In this way hydrazinacetic acid and benzoylhydrazin are formed. By treating the latter with nitrous acid, benzoylazoimid is formed, and by boiling this with alkalies it is decomposed into an alkaline nitride and benzoate. The sodium compound is NaN₂. When this is heated with dilute sulphuric acid the azoimid goes into solution. The solution is strongly acid, and reddens litmus. It has a disagreeable smell, and the vapor given off combines with

*Ber. 20, 1632, and J. prak. Chem. 39, 27.

†Stahl und Eisen, 1890, 1101.

ammonia to form N_2H_4 . Compounds with sodium, potassium, barium, iron, copper, mercury and silver have been prepared. The silver and mercury salts are explosive. We have here a curious instance of two compounds of the same elements, NH_3 and N_2H_4 , one of which is a strong base and the other an acid.

A New Synthesis of Indigo has been effected by Karl Heumann (Ber. 23, 3043) by heating phenyl glyocoll to 260° with 2 parts of caustic potash. Indigo white is obtained in this way, which by solution and exposure to the air is oxidized, and indigo precipitates. The process has been patented by the Badische Anilin u. Soda Fabrik. Biedermann and Lepetit have (Ber. 23, 3289) effected the synthesis in a manner closely resembling this by heating anilin, monochloracetic acid and caustic soda. The yield in this case is only $9\frac{1}{2}$ per cent.

Heliochromes, or Photographs in Natural Colors, are now prepared by F. E. Ives, of Philadelphia, and two samples of pictures on glass by this process were exhibited to the chemists at the Philadelphia meeting. The method is described in the Journal of the Franklin Institute for Jan., 1891. Ives concludes his article with these words: "Composite heliochromy must always remain a comparatively costly process, when carried out in a manner calculated to yield the finest results, and can most profitably be brought before the public in the form of optical lantern lecture illustrations, not with the triple lantern, but with transparent color-print heliochromes mounted as lantern slides. If the color-prints are made by the Woodburytype process, such heliochromic lantern slides, infinitely superior to hand-painted ones, can be made in quantity at a cost not exceeding one dollar each."

PERSONALS.

—Prof. Albert Gallatin has resigned the Chair of Analytical Chemistry, University of the City of New York, and Robert W. Hall, M. D., has been elected to fill the vacancy.

—Prof. P. T. Austen has resigned the Chair of Chemistry in Rutgers College, New Brunswick, N. J.

Obituary.—Jesse Park Battershall. Born May 26, 1851; died January 12, 1891.

=====THE=====

Journal of Analytical AND Applied Chemistry.

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CHEMICAL EXAMINATION OF OSAGE ORANGE (MACLURA AURANTIACA) LEAVES, AND A FEEDING EXPERIMENT IN REARING SILK WORMS.

BY E. A. V. SCHWEINITZ, PH. D.

From Department of Agriculture, Washington, D. C.

For some years the United States Government through the Department of Agriculture has devoted considerable time and money for the purpose of encouraging the rearing of silk worms in this country, and pointing out to the people the best and most economical means of securing good results. The use of the leaves of the osage orange (*maclura aurantiaca*) instead of the mulberry, as a food for the silk worms has been to some extent successfully tried and it was thought advisable to make a chemical study of the value of the osage orange leaves as food and to follow the development of the worm as reared upon this food. This idea was partially carried out in the season of 1889 at the Department.

Already in 1853 and 1859 Peligot presented to certain French scientific societies the results of some chemical and physiological investigations of the food and life of the silk worm. He examined the mulberry leaves. The conclusions drawn by him from the results of his work were that the worms assimilate K_2O , MgO , P_2O_5 , and excrete SiO_2 , $CaSO_4$, and $CaCO_3$. Further, that the worms assimilate some of the nitrogenous material of its food, that there is neither an exhalation of nitrogen, nor an assimilation of atmospheric nitrogen, and that for every 100 parts of carbon assimilated about 50 are used for respiration.

This work was supplemented by an extensive investigation

conducted by Dr. O. Kellner in Tokio, Japan, in 1883, the results of which are published in *Die land. Versuchs station*, Bd. 30, 1884. The food which he examined was also the mulberry. His experiments were made with quite a large quantity of worms, and are therefore of considerable value. Our own experiments were made, as before stated, upon the osage orange and with the Cevennes race of silk worms.

The experiments were begun after the worms had passed through the first moult, as before this they were so exceedingly small that it would have been very difficult to handle them. At this time several lots were selected and weighed and a weighed quantity, after being killed with chloroform, was burnt for the purpose of determining the percentage of ash. The remainder were carefully watched during different stages of growth. The leaves fed to the worms daily were carefully weighed and the same quantity placed for 24 hours by the side of the tray upon which the worms were reared, for the purpose of determining approximately the loss of moisture by spontaneous evaporation. The leaves used for analysis were thus approximately under the same conditions as the food of the worms. The stages in the life of the worms selected for collecting and analyzing the residues were at the moulting times, which occurred at intervals of four to five days. The check samples of leaves, the residue, food left unconsumed, excrement for each stage were then carefully collected, weighed, and submitted to analysis. A weighed quantity of worms was also taken at the end of each moult and analyzed and, as at the beginning, several lots had been selected, it was possible to continue the work with worms which had been under the same conditions as those used. The time from the first moult, at which date the experiment was begun, May 5, till the time for spinning, May 25, was 20 days. The weight of one hundred worms which just after first moult was 0.765 gms. at spinning time was 345.3 gms. Or, taken on the dry substance, 0.1091 gms., being the weight of 100 worms after first moult, the weight at spinning time was 45.822 gms. See Table 1.

In regard to the proximate composition of the osage orange leaves, residue, and excrement, this can be best understood by a glance at Table No. 2. The determinations were made on the

moisture-free samples. The average per cent. of moisture in the fresh leaves was about 78. The large percentages of crude fat and albuminoids are to be especially noted in this connection and the higher percentage of albuminoids in the food of the first moult, corresponding to a younger leaf, and at the time when the worms would apparently require this class of food. As the leaves become older and larger the proportion of albuminoids decreases. The small amount of albuminoids in the excrement shows the assimilation of considerable albuminoid material from the food. The richness of the excrement in crude fiber and ash is what one would naturally expect.

A determination of the percentage of nitrogen in the worms themselves at end of each moult showed :

2d Moult.	3d Moult.	4th Moult.	Spinning.
Per cent. Nitrogen.	Per cent. Nitrogen.	Per cent. Nitrogen.	Per cent. Nitrogen.
14.00	12.98	10.92	9.97

and glancing again at Table No. 2, we note a steady decrease in the amount of albuminoids in the food, as well as in the quantity assimilated.

If we compare these results on osage orange leaves with those obtained by Kellner on mulberry leaves (Table No. 3), we will notice that the leaves examined by him were less rich in albuminoids and fat, but that there was a corresponding decrease in per cent. of albuminoid as the leaf grew. If we calculate the nutritive ratio in accordance with the old method adopted for cattle feeding, we have results given in Table 2 and Table 3. It may be mentioned here that during the last stage of their life a great number of worms died from the diseases of silk worms, called *flacherie* and *graserie*. These diseases are attributed by some to a super-richness of the food, and it would seem that the worms previously reared on mulberry would have to be gradually accustomed to the richer osage orange food. In Tables No. 4 and 5 are given my own and Kellner's results of the ash analyses of leaves, residues, and excrements of the osage and mulberry respectively. Without going into details, it is especially interesting to note the large percentages of phosphoric acid, potash, and magnesia which are absorbed and the excretion of lime and silica.

The presence of boracic acid in the ash of the leaves is also of interest. In 1889 Dr. C. A. Crampton published (in *Ber. d. d. ch. Ges.* XXII, p. 1073)* an article on the occurrence of boracic acid in the ash of plants. He, as well as Baumert, found it as a normal constituent of wines, and Crampton and Knorr also detected boracic acid in the ash of watermelons, peach leaves, peach stems and the fruit. Hence we would suggest again, as has been done by others, the advisability of examining the ash of plants in general for boracic acid. I hope in the near future to be able to make a quantitative determination of the boracic acid in the ash of the osage orange.

The analyses presented in the tables also show the change in the constituents of the osage leaf during growth from May 2 to May 25. It was the intention to study these constituents from the time the leaves begin to bud until the late fall. The samples of leaves were collected for this purpose. It was further the purpose to study more closely the proximate constituents of the leaves of osage and mulberry and determine what, some at least, of the substances we class as crude fats, carbohydrates, albuminoids, etc., really are.

Other more important work has interfered with the accomplishment of this plan up to the present, but I hope to be able to complete it. So much, however, I have already determined, viz., that both the mulberry and osage orange leaves contain substances of an alkaloidal character. So far as the value of the orange leaves as food for worms is concerned, the food is richer than the mulberry, and the high percentages of potash, phosphoric acid, and magnesia are characteristic both of mulberry and osage, with large excess in favor of the latter. That these substances are essential for the worms can be seen from an analysis of the ash of the worm, Table 4.

Some of the conclusions of Kellner, partially confirmed by my work from a study of the tables, may be added here, viz.: That silk worms are not able to digest crude fiber; that the nitrogen free material is much less digestible for them than for the higher orders of animal life; that of the nitrogenous substances of the food, the albumen is the more useful to the worms; that

*See also this Journal 4, 191.

they neither assimilate nor excrete nitrogen as a gas or as gaseous compounds. As Regnault & Reiset* have observed, the digestive processes are more rapid in insects than in other lower animals. 1 kg. silk worms after the second moult exhale 1.19 gm. CO₂, and at the end of their life 0.73—1.321 gm. per hour. As Henneberg, Soxhlet and Schulze, and others, have shown for the higher animals, so is there in the lower animals, from a food rich in nitrogen, a formation of fat from nitrogenous free substances, even when the food is rich in nitrogen.

Table 1. *Weight of Worms, Residue, and Excrement.*

	Taken after First Moul.	Taken after Second Moul.	Taken after Third Moul.	Taken after Fourth Moul.	Taken after Spinning.
Weight of 100 worms :					
Fresh grams.	0.765	3.450	17.395	81.809	345.300
Dry "	0.1091	0.460	1.898	13.741	45.822
Per cent. of ash	9.10	13.81	17.59	12.42	10.38
Per cent. of moisture	86.67	89.04	84.39	86.73

Table 2. *Proximate Composition of Osage Orange Leaves, etc.*

	LEAVES.				RESIDUE.			EXCREMENT.		
	First to Second Moul.	Second to Third Moul.	Third to Fourth Moul.	Fourth to Spinning.	Second to Third Moul.	Third to Fourth Moul.	Fourth to Spinning.	Second to Third Moul.	Third to Fourth Moul.	Fourth to Spinning.
Petrol'm ether extract	9.86	9.51	12.24	12.26	9.67	8.21	9.53	10.88	8.10	7.97
Ether extract	9.25	9.01	10.01	9.16	9.93	8.21	7.30	9.59	7.75	7.48
Albuminoids	33.93	31.31	26.40	18.87	29.37	24.12	20.31	21.52	19.25	16.12
Carbohydrates, starch, etc., by difference .	27.26	30.36	19.68	20.33	31.83	20.05	21.11	19.69	10.25	22.67
Ash	9.87	11.60	10.52	10.06	10.36	10.02	8.45	12.47	12.16	10.75
Crude fiber	8.83	8.21	21.02	28.29	8.84	29.39	33.30	25.85	42.49	35.01
95% alcohol extract .	26.69	28.63	18.27	19.29	30.00	18.61	20.16	18.22	9.19	18.69
Nutritive ratio . .	1:1½	1:2	1:2½	1:4						

*F. Hoppe-Seyler, *Physiol. Chem.* III, Phil. 1879, p. 530.

Table 5. Composition of the Ash of Mulberry Leaves.

	LEAVES.		RESIDUE.		EXCREMENT.	
	Third to Fourth Moul.	Fourth Moul. to Spinning.	Third to Fourth Moul.	Fourth Moul. to Spinning.	Third to Fourth Moul.	Fourth Moul. to Spinning.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
Silicic acid	18.03	25.03	19.38	22.06	19.09	30.32
Sulphuric anhydride	2.95	2.05	2.97	1.92	3.10	2.72
Phosphoric acid	8.28	5.96	5.84	6.22	7.06	4.84
Chlorine	0.39	0.69	0.38	0.71	0.39	0.96
Lime	33.48	30.39	32.22	29.25	35.55	30.01
Magnesia	8.00	10.64	8.02	9.20	6.55	9.56
Soda	1.24	1.82	1.40	2.84	1.32	1.65
Potash	26.43	21.95	28.70	26.33	24.42	18.39
Iron oxide	1.72	1.43	1.87	1.31	1.43	1.49

THE EFFECT OF AMMONIA SALTS ON THE PRECIPITATION OF ZINC AS PHOSPHATE.

BY GEO. C. STONE.

In a paper, on the Determination of Manganese and Zinc as Pyrophosphates,* Mr R. C. Boyd says that he found that large amounts of ammonia salts interfered with the precipitation of zinc, and that the precipitate was much more soluble in a hot solution of ammonium chloride than in a cold one. Having used this method of precipitation for several years without noticing anything of the kind I made some experiments to test the matter. When I first tried the method I found that it was necessary to use a very large excess of the precipitant in order to insure complete precipitation; on reading Mr. Boyd's paper it at once occurred to me that possibly his trouble was due to his not having used enough. The following experiments I think will show that this was probably the case.

The analyses were all made by adding a solution of the ammonia salt to a solution containing a known amount of zinc, adding a measured amount of a ten per cent. solution of microcosmic salt, (called throughout this paper Sph. sol.† for brevity) diluting to

*School of Mines Quarterly. Vol. XI. p. 355.

†Salt of Phosphorus.

about 300 cc., adding ammonium hydroxide till the precipitate at first formed redissolved, then acetic acid till just distinctly acid to litmus paper,* heating on the water bath until the bulky flocculent precipitate at first formed became dense and crystalline. In some cases the precipitate was filtered from a hot solution, in others it was allowed to cool first, in all cases it was thoroughly washed with hot water, dried and ignited with the necessary precautions.

The $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ used for all the analyses I tested by making two analyses by exactly the same method as used in trying the effect of ammonia salts. For the first I used 35 cc. Sph. sol. and filtered cold, found .3413 gms. zinc; for the second I used 50 cc. Sph. sol. and filtered hot, found .3411 gms. zinc. The zinc by calculation from the amount of sulphate taken was in each case .3412 gms.

To see if there was any possibility of error from using an excess of Sph. sol. I took two lots of 0.5 gms. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and added 30 gms. Sph. dissolved in about 200 cc. of water to each, diluted to about 300 cc. and precipitated as usual. The precipitate was unusually fine, settled badly, filtered slowly and ran through on washing. I let the filtrates stand till the precipitates had settled, filtered, washed and dissolved the precipitates in dilute nitric acid, evaporated and ignited, found

Main precipitate, .1100 gms. zinc.	Precipitate from filtrate, .0031 gms. zinc.
" " .1105 "	" " " .0018 "

Total .1131 and .1123 gms. zinc; the theoretical amount is .1132.

The first was filtered hot, the second cold. As the amount of Sph. used in these two experiments was about one hundred times what is theoretically necessary there is evidently no danger of error from using a large excess.

Took five lots of zinc sulphate, each containing .3412 gms. zinc, added to each 10 gms. NH_4Cl . Theoretically this amount of zinc requires 11 cc. Sph. sol. to precipitate it. To the first I added 15 cc., found .3219 gms. zinc, .0193 gms. low. To the second I added 20 cc. Sph. sol., found .3392 gms. zinc, .0020 gms. low. To

*An excess of one or two cc. of acetic acid does no harm but more dissolves rapidly increasing amounts of the precipitate until with about 20 cc. it is completely dissolved.

the third I added 25 cc. Sph. sol., found .3396 gms. zinc, .0016 gms. low. The filtrates from all three gave precipitates with $(\text{NH}_4)_2\text{S}$ at once. To the fourth and fifth lots I added 50 cc. Sph. sol., gave .3422 and .3419 gms. zinc, .0010 and .0007 high. All five were filtered hot.

Two lots each containing .3412 gms. zinc; added 35 gms. NH_4Cl and 35 cc. Sph. sol. (1 cc. for each .01 gms. zinc). The first filtered cold gave .3407 gms. zinc, .0005 gms. low; the second filtered hot gave .3417 gms., .0005 high.

To see if the completeness of the precipitation was due to the absolute or relative amount of Sph. present I took four lots of .3, .6, .9 and 1.2 gms. zinc sulphate, added to each 25 gms. NH_4Cl and Sph. sol. in the proportion of 1 cc. for each .01 gm. zinc, filtered them all cold and found :

Zinc taken, .0679 cc.	Sph. used, 7.	Zinc found, .0675.	Difference, —.0004.
" .1359 "	" 14.	" .1360.	" +.0001.
" .2038 "	" 21.	" .2052.	" +.0014.
" .2718 "	" 28.	" .2724.	" +.0006.

The solubility evidently does not depend on the absolute amount of Sph. present or on its ratio to the ammonium chloride.

Took .3412 gms. zinc as sulphate, added 13 gms. ammonium acetate, 35 cc. Sph. sol., filtered cold, gave .3420 gms. zinc.

Two lots, each containing .3412 gms. zinc, added to each 48 gms. ammonium acetate and 35 cc. Sph. solution. The first, filtered cold, gave .3404 gms. zinc, .0008 gms. low; the second, filtered hot, gave .3388 gms. zinc, .0024 gms. low.

Took two lots each .3412 gms. zinc, added to each 48 gms. ammonium acetate and 10 gms. ammonium chloride, 35 cc. Sph. sol. The first, filtered cold, gave .3398 gms. zinc, .0014 gms. low; the second, filtered hot, gave .3389 gms. zinc, .0023 gms. low.

Took four lots of zinc sulphate, added to each 25 gms. ammonium acetate, and Sph. sol. in the proportion of 1 cc. for every .01 gm. zinc present, found.

Zinc taken, .0679 cc.	Sph. used, 7.	Zinc found, .0664.	Difference, —.0015.
" .1359 "	" 14.	" .1356.	" —.0003.
" .2038 "	" 21.	" .2041.	" +.0003.
" .2718 "	" 28.	" .2727.	" +.0009.

All four were filtered cold. As the first was low, I tried two more lots with the same amount of zinc and ammonium acetate, adding 10 cc. Sph. to the first, and filtering cold, found .0661 gms. zinc. —.0018. Added to the second 14 cc. Sph. and filtered hot, found .0667 gms. zinc. —.0012.

The zinc ammonium phosphate is evidently somewhat soluble in a strong hot solution of ammonium acetate ; but apparently not in a cold one, unless there is a very small amount of zinc and a large amount of the ammonia salt.

Took .3412 gms. zinc as sulphate, added 35 gms. ammonium nitrate and 35 cc. Sph., filtered cold. I found that the NH_4NO_3 was not pure, but contained lime. I determined the amount, and after deducting it, found .3419 gms. zinc, +.0007 gms.

Tried two more lots of .3397 gms. zinc each, added 35 gms. ammonium nitrate and 35 cc. Sph. The first, filtered cold, gave .3407 gms. zinc, + .0010 ; the second, filtered hot, gave .3416 gms. zinc, + .0019.

Tried two lots of .3397 gms. zinc with 35 gms. ammonium sulphate and 35 cc. Sph. The first, filtered cold, gave .3399 gms. zinc, + .0002 ; the second, filtered hot, gave .3406 gms. zinc, + .0009.

I think it is safe to conclude from these experiments, that, if as much as three times the theoretical amount of Sph. is used for precipitating, there is no danger of the precipitate being dissolved to any serious extent by any amount of chloride, sulphate or nitrate of ammonia likely to be present. The acetate, especially in a hot solution, appears to dissolve more ; and therefore it is better, if there is much free ammonia present, either to evaporate it off, or to nearly neutralize with sulphuric or nitric acid and then make slightly acid with acetic.

The following table gives the results in detail :

Ammonia Salt Added.	Gms.	cc. Sph. Used.	Filtered.	Gms. Zn ₂ P ₂ O ₇ Found.	Zinc Found.	Zinc Taken.	Difference.
		35	Cold	.7981	.3413	.3412	+.0001
		50	Hot	.7977	.3411	.3412	-.0001
		300	Hot	.2646	.1131	.1132	-.0001
		300	Cold	.2628	.1123	.1132	-.0009
Chloride . . .	10	15	Hot	.7528	.3219	.3412	-.0193
" . . .	10	20	Hot	.7933	.3392	.3412	-.0020
" . . .	10	25	Hot	.7942	.3396	.3412	-.0016
" . . .	10	50	Hot	.8003	.3422	.3412	+.0010
" . . .	10	50	Hot	.7997	.3419	.3412	+.0007
" . . .	35	35	Hot	.7991	.3417	.3412	+.0005
" . . .	35	35	Cold	.7967	.3407	.3412	-.0005
" . . .	25	7	Cold	.1579	.0675	.0679	-.0004
" . . .	25	14	Cold	.3181	.1360	.1359	+.0001
" . . .	25	21	Cold	.4799	.2052	.2038	+.0014
" . . .	25	28	Cold	.6372	.2724	.2718	+.0006
Acetate . . .	13	35	Cold	.7999	.3420	.3412	+.0008
" . . .	48	35	Cold	.7960	.3404	.3412	-.0008
" . . .	48	35	Hot	.7923	.3388	.3412	-.0024
" . . .	48						
Chloride . . .	10	35	Cold	.7947	.3398	.3412	-.0014
Acetate . . .	48						
Chloride . . .	10	35	Hot	.7925	.3389	.3412	-.0023
Acetate . . .	25	7	Cold	.1553	.0664	.0679	-.0015
" . . .	25	14	Cold	.3171	.1356	.1359	-.0003
" . . .	25	21	Cold	.4775	.2041	.2038	+.0003
" . . .	25	28	Cold	.6380	.2727	.2718	+.0009
" . . .	25	10	Cold	.1545	.0661	.0679	-.0018
" . . .	25	14	Hot	.1560	.0667	.0679	-.0012
Nitrate . . .	35	35	Cold	.7997	.3419	.3412	+.0007
" . . .	35	35	Cold	.7968	.3407	.3397	+.0010
" . . .	35	35	Hot	.7990	.3416	.3397	+.0019
Sulphate . . .	35	35	Cold	.7950	.3399	.3397	+.0002
" . . .	35	35	Hot	.7965	.3406	.3397	+.0009

BORAX IN CALIFORNIA.

The following interesting account of the extraction of borax in California is taken from the report of the State Mineralogist, Wm. Ireland, Jr., for 1890. The description of the borax marsh in San Bernardino County is written by Dr. Henry De Groot and of the Lake County deposits by Mr. W. A. Goodyear. Both of these

gentlemen are assistants on the staff of the State Geological Survey.

THE SEARLES BORAX MARSH.

PLANT, PROPERTY, AND OPERATIONS OF THE SAN BERNARDINO BORAX COMPANY.

This marsh is situated in the northwestern corner of San Bernardino County, occupying a portion of T. 25 S., R. 43 E., M. D. M.

The site is distant from San Francisco southeast five hundred miles; from San Bernardino, the shire town of the county, due north one hundred and seventy-five miles; and from Mojave, nearest station on the Southern Pacific Railroad, northeast seventy-two miles; these distances being measured by the usually traveled routes.

Difficulty and Dangers of Travel.—Arriving at Mojave, the rest of the way must be made by team, no stage running over this portion of the route. There are, in fact, no stages or other public conveyances to be found in any part of this county.

If the distance is long, it cannot be made on horseback, owing to want of feed and water, whatever the route pursued. The stranger here should not undertake any long journey without a guide, as he will encounter many branch and cross-roads that may easily be mistaken, and the wagon-tracks, especially along the "washes," become often obscured or completely obliterated by the drifting sand or by the sediment brought down from the mountains by rain, leaving the bewildered traveler at a loss which way to go. The distances on the deserts are also delusive. The very land-marks adopted for our guidance prove deceptive, the contour of mountains changing as we approach them or as we look at them from a different point of view. The inexperienced traveler, if he has far to go, will therefore consult both his safety and his comfort if he takes with him some one acquainted with the roads and familiar with life on the desert.

When and by Whom Discovered.—This extensive and valuable deposit of borax was discovered by John W. Searles, who first observed signs of this salt when crossing the marsh that now bears his name, in 1862, at which time he was engaged in prospecting for gold in the Slate Range lying to the east.

Being unacquainted with the nature of the substance, he did not at the time pay much attention to it. Afterwards, however, when borax began to be an object of general inquiry, he recognized in some samples of this salt shown him the stuff he had noticed while crossing the alkaline flat several years before. Satisfied on this point, he at once took proper steps for locating such portions of the marsh as he considered most valuable.

Its Physical Peculiarities and Probable Origin.—Locally considered, Searles Marsh lies near the center of an extensive mountain-girdled plain, to which the phrases "Alkali Flat," "Dry Lake," "Salt Bed," and "Borax Marsh" have variously been applied, the contents and physical features of this basin-shaped depression well justifying the several names that have so been applied to it. It is, in fact, a dry lake, the bed of which has been filled up in part with the several substances named. Its contents do, in reality, consist of mud, alkali, salt, and borax, largely supplemented with volcanic sand. This depression, which has an elevation of 1700 feet above sea level, and an irregular oval shape, is about ten miles long and five miles wide, its longitudinal axis striking due north and south. It is surrounded on every side but the south by high mountains, the slate range bounding it on the east and north, and the Argus range on the west, the view to the south being shut out by low mountains, conical peaks, and broken hills which break away to the southeast. Conspicuous in that direction stands a series of splintered buttes, so slender and pointed that the name "needles" has been applied to them.

No doubt but this basin was once the bed of a deep and widely extended lake, the remains of a former inland sea. The shore line of this lake is distinctly visible along the lower slopes of the surrounding mountains at an elevation of 600 feet above the surface of the marsh. Further up, one above the other, faint marks of former water lines can be seen showing the different levels at which the surface of the ancient lake has stood. In the course of time this lake was extinguished, having been filled up with the wash from the adjacent mountains, originally much taller than they are to-day. What may have been the depth of this lake has not yet been ascertained, borings put down 300 feet having failed to reach bed rock.

What the Artesian Auger Reveals.—The borings mentioned, commenced in 1887, disclosed the following underlying formations, the successive strata having been observed and noted by Superintendent Searles, who had the work in charge :

1. Two feet of salt and thenardite.
2. Four feet of clay and volcanic sand, containing a few crystals and bunches of hanksite.
3. Eight feet of volcanic sand and black, tenacious clay, with bunches of trona, of black, shining luster, from enclosed mud.
4. Eight-foot stratum, consisting of volcanic sand containing glauberite, thenardite, and a few flat hexagonal crystal of hanksite.
5. Twenty-eight feet of solid trona of uniform thickness—other borings showing that this valuable mineral extends over a large area.
6. Twenty-foot stratum of black, slushy, soft mud, smelling strongly of hydrosulphuric acid, in which there are layers of glauberite, soda, and hanksite. The water has a density of 30° Beaume.
7. Two hundred and thirty-feet (as far as explored) of brown clay, mixed with volcanic sand and permeated with hydrosulphuric acid. Overlying number five a thin stratum of a very hard material was encountered. Being difficult to penetrate, and its character not recognized, this was simply called "Hard Stuff," its more exact nature being left for future determination.

How Fertilized and Filled Up.—Whatever the agencies that in the first place scooped out the bed of this lake, or however it came afterwards to be drained of its waters, the process by which it has since been filled up, as well as the sources of its wonderful enrichment, is well understood. The rocks of the surrounding region being mainly of volcanic origin, abound with the various salts found in this marsh. As these rocks have undergone decomposition, these salts, set free, have mingled with and become constituent parts of the soil. The rains falling on this soil have carried it, together with the salts it contained, down and deposited it in this central basin, filling it up to the extent we now see. That this filling-up process must have been slow in a climate marked by such extreme aridity, admits of no question. The

wash from the water-shed of this basin is not large, and would have been extremely limited but for the cloud-bursts that occasionally occur on the surrounding mountains, and which in former times were probably heavier and of more frequent occurrence than at present.

Only in excessively wet winters do more than a few small streams flow down the ravines eroded in the rim of this basin, and these dry up almost as soon as the rain ceases to fall. But the filling up of this ancient lake has not been due solely to the soil washed in by the surface water. It has been greatly hastened by the large quantities of dust and sand swept in by the strong winds that blow here periodically from the west.

While the solfataric action may have had something to do with the production of these salts, that their presence here is mainly, if not wholly, due to the source above indicated, can hardly be questioned.

By some it is thought that the drainage of Owens Valley, a long depression lying to the north, flows this way. Should this be the case, the waters from that valley may have contributed much towards fertilizing this marsh, as they traverse a region largely composed of volcanic rocks. This hypothesis, however, seems to the writer more than problematical, much hilly and even mountainous country interposing between these points. As is the case with all salines of like character, this has no outlet. The water that comes into it can escape only by evaporation, which process goes on here very rapidly for two-thirds of the year. While most of the water contained in this basin is subterranean, a little during very wet winters accumulates and stands for a short time on portions of the surface. In no place, however, does it reach a depth of more than a foot or two, hardly anywhere more than three or four inches.

Within the limits of the actively producing portion of the marsh, which covers an oblong area of about one thousand seven hundred acres, the water stands on a tract of some three hundred acres for a longer period than it does elsewhere, but even here it nowhere reaches a depth of more than one foot.

Between this three hundred acre tract and the main flat, lying a little lower, there interposes a slight ridge which prevents the surface water from escaping to the lower ground.

This entire productive section is, in fact, slightly depressed below the general level of the flat, to which circumstance, no doubt, its greater fertility is due. As certain degrees of moisture are necessary to maintain the process of capillary attraction, this goes on at this lower point, to which the water gravitates with greater steadiness and activity than elsewhere. After a slight winter rainfall, causing the water to subside to an unusually low level, the restoration of these surface deposits go on slowly, and may even be wholly arrested.

The Various Mineral Substances Found Here.—This water, which is of a dark-brown color, and strongly impregnated with alkali, has a density of 28° B. The salts obtained from it by crystallization contain carbonate, chloride, and baborate of sodium, with a large percentage of organic matter.

Summarized, the following minerals have been found associated with the borax occurring in the Searles Marsh: Anhydrite, calcite, celestite, cerargyrite, colemanite, dolomite, embolite, gaylussite, glauberite, gold, gypsum, halite, hanksite, natron, soda, nitre, sulphur, thenardite, tincal and trona, the most of them occurring, of course, in only minute quantities. There is, however, reason to believe that hanksite will yet be found abundantly, both here and in the other salines of this region.

The submerged tract above described is called the "Crystal Bed," the mud below the water being full of large crystals, which occur in nests at irregular intervals to a depth of three or four feet; many of these crystals, which consist of carbonate of soda and common salt, with a considerable percentage of borax, are of large size, some of them measuring seven inches in length. The water 15 feet below this stratum of mud contains, according to Mr. C. N. Hake, who made, not long since, a careful examination of these deposits, carbonate of soda, borax, and salts of ammonia. The ground in the immediate vicinity, a dry hard crust about one foot thick, contains, on the same authority:

Sand	50 per cent.
Sulphate of Soda	16 "
Common Salt	12 "
Carbonate of Soda	10 "
Borax	12 "

The borax here occurs in the form of borate of soda only, no ulexite (borate of lime) having yet been found.

How Gathered, and How the Crust Produces Itself.—It is the overlying crust mentioned that constitutes the raw material from which the refined borax is made. The method of collecting it is as follows: When this crust, through the process of efflorescence, ever active here, has gained a thickness of about one inch, it is broken loose and scraped into windrows far enough apart to admit the passage of carts between them, and into which it is shoveled and carried to the factory located on the northwest margin of the flat, one to two miles away.

As soon as removed, this incrustation begins again to form, the water charged with the saline particles brought to the surface by the capillary attraction evaporating and leaving these particles behind. This process having been suffered to go on for three or four years, a crust thick enough for removal is again formed; the supposition being that this incrustation, if removed, will, in like manner, go on reproducing itself indefinitely. In order to determine the proportionate growth of the various salts contained in this crust while undergoing this recuperative process, Mr. Hake took samples representing, respectively, six months, two, three and four years' growth. From the ground from which these samples were taken, the crust had been removed several times during the preceding twelve years.

The analysis of these samples gave the following results:

	Six Months' Growth.	Two Years' Grqwth.	Three Years' Growth.	Four Years' Growth.
Sand	58.0	55.4	52.4	53.3
Carbonate of Soda	5.2	5.0	8.1	8.0
Sulphate of Soda	11.7	6.7	16.6	16.0
Chloride of Sodium	10.9	20.0	11.1	11.8
Borax	14.2	12.9	11.8	10.9
Totals	100.0	100.0	100.0	100.0

From this list it will be seen that the first six months' growth is richest in borax, and that the proportion of carbonate of soda to borax increases regularly. The presence of so much sand as is

here indicated is caused by the high winds that blow at intervals, bringing in great quantities of that material from the mountains to the west. This sand, it is supposed, facilitates the formation of the surface crust by keeping the ground in a porous condition.

Character and Capacity of Works.—The works erected here are capable of turning out over one hundred tons of refined borax per month. They are, however, not run to their full capacity, a slightly restricted production having been found expedient. Besides being extensive, these works are very complete in all their appointments, the several departments consisting of a concentration, a refining, and a boiler house.

For doing the moving and hoisting, derricks, tramways, and similar appliances are provided, every labor-saving device known having been introduced here. Shops and outbuildings of all needed kinds, a cooperage and warehouse, dwellings for Superintendent and workmen, barn, sheds, stables, corrals, etc., are all on the premises.

Process of Manufacture.—The crude stuff having been collected on the marsh and hauled to the factory in the manner stated, is thrown on the dumping ground close by, a stock of several thousand tons being kept constantly on hand. As required the material is carted into the works and thrown into dissolving tanks filled with a boiling saline solution, and there kept until it is completely dissolved, free ammonia being meantime copiously given off. The heat supplied to the tanks consists of steam passed through a coil placed near their bottoms, this coil being pierced with many minute holes for the escape of the steam. The various salts being dissolved, there is left at the bottom of the tank an insoluble residue, chiefly mud and sand. The hot solution, having been left about eight hours to settle and clarify, is run off into long wooden crystallizing tanks and allowed to cool, which requires from five to nine days according to the temperature of the air. The product of the first crystallization is a somewhat impure article of borax, slightly discolored by organic matter, and which is either sold as concentrates or redissolved in boiling mother liquor, and the resultant solution allowed to cool to 120° F. From the solution thus obtained borax of a superior quality is made.

By a system of careful experimentation kept up for a year, the Superintendent of the works, Superintendent Searles, has succeeded in extracting the borax from the crude material treated up to a high percentage, very little of the salt being lost. The wooden dissolving tanks now in use are about to be replaced by larger ones made of iron with steel bottoms.

Fuel and Water Supply.—The fuel formerly used in these works consisted of greasewood and sagebrush, the only kinds found in the country. No trees grow here. For about three years an acceptable substitute for these shrubs has been found in crude petroleum, which, besides proving far more economical and less troublesome, affords a steadier heat.

The water used here for drinking and for feeding the boilers is obtained from a group of springs seven and one half miles distant in the Argus Mountains, whence it is brought in through iron pipes, being delivered at the works under a thousand foot head. It is abundant and of excellent quality, being soft and pure. The water required for other purposes is delivered from artesian wells, of which fourteen, sunk on the border of the marsh to a uniform depth of fifty-five feet, affords an ample supply. This water which flows steadily rising from 5 to 10 feet above the surface, contains about one per cent. of carbonate of soda, strong traces of borax, and salts of ammonia equal to about 18 grains per gallon. It answers well for dissolving the crude material and for most other uses about the works in which the consumption is large.

Labor and Transportation.—The company employs about thirty men in the several departments of the business. Fifty animals, mostly heavy draft mules, are required for the transportation service, which includes hauling the raw material from the marsh to the factory and the manufactured article from the latter to Mojave, shipping and receiving point on the Southern Pacific Railroad. Transportation to Mojave is performed with twenty-mule teams, attached to two sets of wagons capable of carrying a total of fifteen tons. Returning, these teams bring back such supplies as the company requires, including the crude petroleum used for fuel, one trip being made every eight days.

BORAX LAKE, LAKE COUNTY.

Situated about a half mile east of the lower end of Clear Lake

is a pond, the water of which is highly charged with the biborate of soda. During the dry season this water mostly disappears, through evaporation, and the borax crystallizing out is found in the mud on the margin of the pond. Twenty-five years ago large quantities of this salt were manufactured here, the first made in the United States is said to have been produced at this place. There has, however, no work been done here for a long time, the business having been given up on the discovery of more extensive and productive salines in the southern part of the State and in Nevada.*

Some years since there was a considerable rise in the water of Borax Lake, supposed to have been due to the rise in the waters of Clear Lake, which was produced by a dam built by certain parties across the head of Cache Creek, just at the outlet of the lake.

The extraction works of the Borax Company were built at a low level close to the margin of the lake, and the rise of the latter was sufficient at one time to flood some of their furnaces and cause them serious trouble. The extraction works here were extensive, and involved the expenditure of large sums of money. Mr. Anthony McCabe informed me that the borax company owned about two thousand eight hundred acres of land on this peninsula, between the two arms of Clear Lake, including the Sulphur Banks at the head of the eastern, or shorter arm of the lake, which they rented to other parties, who successfully extracted a large amount of sulphur there.

Before the company ceased operating at Borax Lake, they had, he says, pretty well exhausted the layer of borax crystals which formerly existed in the bed of the lake, and had erected extensive works with a view to extracting the borax from the general mass of the mud of the lake. But these works did not prove a success. Shortly afterwards there was again a rise in the water of the lake which flooded the furnaces, and the work stopped and has not since been resumed.

It is stated that it was found impracticable by simple treatment with water alone to extract from the clayey mud all of the borax which it contained. It was therefore inferred that the mud needed a previous "roasting," and extensive works were erected for this reduction. The mud extracted from the bed of the lake by a

*This paragraph is taken from the State Report for 1888.

dredging machine was first exposed to the action of the atmosphere and the summer sun until thoroughly aerated, and afterwards conducted to the "roasting" arrangement. This arrangement consisted of a rectangular brick chamber in which the dried mud was exposed for a certain length of time to the action of warm, moist air driven through it by a fan-blower, the air being heated and moistened by a small jet of steam turned into the feed pipe from a boiler near at hand. This constituted the roasting.

After being subjected to this treatment for a certain length of time it was removed from the chamber and treated with hot water to dissolve out the borax, the water after a time being drawn off and the residual mud thrown away.

I give the outline of the above so-called "roasting" operation as I received it, and cannot, of course, vouch for its accuracy; but judging as well as I could from the buildings and arrangements which were erected for the especial purpose of extracting the borax from the mud, these appear to have been designed and built with especial reference throughout to exactly the sort of silly "roasting" described above. I am strongly inclined therefore to believe the statement correct, although I should decidedly prefer to believe otherwise, for, indeed, it seems hardly credible that a company of intelligent individuals should have expended from \$75,000 to \$100,000 in the erection of buildings and apparatus for a process of borax extraction which was to any extent dependent for its success upon the results of a "mud-roasting" process like this.

Two or three wells have been bored to some depth in the bottom of the lake in the hope of finding stronger borax solutions. It is stated that from one of these wells all the water obtained was weaker than the water of the lake. In another one, however, there was found at the depth of sixty feet a solution which was considerably stronger than the lake, but in the same well, on going deeper, the solution obtained from a depth of one hundred feet was not so strong.

This process of steaming and lixiviation was the last one tried here, and it was stated to be a failure, in as much as it did not extract from the mud anything like the quantity of borax which analysis showed it to contain. But I do not know why it should not be practicable to extract all of the borax from the fresh mud

by simple lixiviation with hot water. The company is said to have extracted some five or six hundred tons of borax.

LITTLE BORAX LAKE, LAKE COUNTY.

Little Borax Lake occupies the lowest portion of the little basin immediately southeast of the saddle which connects Elgin's Point with the main mountain, and close to the shore of Clear Lake. At the time of my visit they were extracting, with apparent success, the borax from the water of this little lake. It was stated to me here that the density of this water was about 8° B., that of the water of Borax Lake being between 3° and 4° B. It was further stated that the mixture of salts contained in the latter consisted of from 25 to 30 per cent. of borax, the remainder being chiefly carbonate of soda, with, however, about 8 per cent. of common salt.

If these statements be correct, it would follow from them: first, that the water of Little Borax Lake contains between two and three times as much solid matter as that of Borax Lake; second, that of this solid matter the percentage of borax, though nearly the same, is, nevertheless, a little higher at the little lake; and third, that at the latter locality there is far more carbonate of soda and far less chloride of sodium than at Borax Lake. I find however, that the sample of water at Borax Lake which was analyzed by Mr. Moore (see *Geology of California*, Vol. I, p. 98.) possessed a specific gravity more nearly approximating this than three or four degrees Beaume, but what changes may have subsequently taken place in its density, in connection with its changes of level, I do not know.

The water at the little lake was first concentrated by solar evaporation in large areas floored or paved with brick, a brick margin being raised around the edges sufficiently high to hold the water to a depth of a few inches, and the whole surface being covered with asphalt to render it water tight. When the concentration had reached a certain point, the water was drained off from these vats and further concentrated to saturation by boiling. The hot saturated solution of mixed salts was then placed in tin milk pans and cooled and crystallized. Hundreds of these pans were used. After crystallization, the water from them was drawn away and the salts were washed with cold water, which readily dissolves carbonate of soda and common salt, but comparatively

little of the borax. The washed borax was then redissolved in boiling water, and the hot saturated solution thus obtained run into large wooden vats in which it slowly cooled, and the borax crystallized in the interior of the vats and on numerous strings which were suspended in the solution from sticks laid across the tops of the vats.

The carbonate of soda was afterwards purified from the salts which it contained.

THE "IOWA STATION MILK TEST." *

A NEW DAIRY TEST FOR DETERMINING THE AMOUNT OF BUTTER FAT IN MILK.

BY G. H. PATRICK.

1. Introduction. *Testing Dairy Cows—*

During the spring of 1889, while engaged in analyzing the milk of the college herd, I was impressed anew with the very great need, long felt by farmers, dairymen and breeders, of a speedy, easily worked, inexpensive and reasonably accurate method for testing the quality of milk—a method capable of being executed by anyone at home, in the dairy or in the farmer's kitchen, and which would enable the milk producer or the breeder to determine, at trifling expense, the yield of butter fat (or milk fat) from the individual cows of the herd.

That great differences often prevail among the cows of a herd, as regards the butter making quality of milk produced, is well known; likewise that *breed is not a guarantee of quality*—the difference between two cows of the same breed being frequently as great as between the averages for different breeds, even for those of very unlike average quality.

So it is regarding the actual, or possible, butter product for the year, of herd or animal—it depends upon *individual* peculiarities or tendencies, which vary widely within the same as well as among different breeds.

It is therefore most important, especially in these times of low priced farm products and narrow margins of profit, for the man whose profit lies in the conversion of hay and grain into butter fat, through the agency of his dairy herd, to make sure that *every animal which he feeds* is qualified in a high and *profitable* degree to effect that transformation.

*From Bulletin No. 8 of the Iowa Agricultural Experiment Station.

Without doubt a very large number of the dairy cows of this State and of the country at large are kept at a positive loss. How many such there are, or what proportion their number bears to the total number of dairy cows, it is impossible to say with much certainty; but it has been estimated by persons competent to judge, that at present prices of dairy products their proportion probably reaches one-fourth of the entire number. If this estimate be correct it means more than appears at first glance; it means that *one-half the dairy cows are kept without profit; for the one-fourth kept at a loss eat up the profits of another one-fourth!*

This may be an exaggerated view of the case, based upon too high an estimate, but putting the proportion kept at a loss as low as one-sixth, which is probably below the truth, we have then one-third of the dairy cows kept without profit. In other words, competent judges estimate that one-half, or at the lowest one-third, of the capital invested in dairy stock is *dead capital*—unproductive!

Such a state of things should arouse farmers, dairymen and stock breeders to action; effective action in this case means detection of the unprofitable animals and weeding them out of the herd—turning them into beef.

How shall the unprofitable animals be detected?

How shall the relative productiveness, in butter, of the individual cows be ascertained?

In either of two ways:

1st. By setting each cow's milk by itself, skimming, ripening and churning the cream separately—and repeating the operation several times during the year.

2d. By determining the amount of butter-fat in each cow's milk (morning's and night's mixed) several times a year by a simple dairy test—a daily record being also kept of the quantity of milk given by each cow.

The amount of work involved in the first method is so great as to render it almost impracticable with a herd of any considerable size.

Among the approved methods for sifting the dairy herd I do not include the rather popular "cream test"—measurement of the volume of cream thrown up by the milk when set in narrow tubes—because exact experiments made in late years have shown this method to be unreliable and often seriously misleading. Many

investigations prove this. Among the latest of these was a very extensive and laborious one conducted at the Kansas Experiment Station, lasting from July 15th to September 9th (1888), in which six cows were submitted to trial, in pairs, the morning and evening milk being tested (i. e. analyzed), creamed and churned, separately. The teachings of this experiment are so plain, they are so clearly and forcibly set forth in the report, and are in themselves so valuable as a means of correcting a popular erroneous idea, that I will digress from my main subject long enough to quote from Prof. Shelton's report of the experiment, as follows: (First Annual Report of the Kansas Experiment Station, pp. 92-93.)

"Popularly the notion is held, that the cream yielded by milk is a safe index of its butter capacity. It is of course true that rich milk throws up heavy and abundant cream, while thin and watery milk gives a light skimming of cream; but what is plainly not true, according to the facts of this experiment, is the assumption that the milk is valuable in proportion to the cream it yields, implying that cream is everywhere alike in value. In the common practice of buying cream by the "gauge," it is supposed that the product of cream in butter is uniform. In this experiment of ours, cream was the one discordant element. In the case of every cow employed, and with each kind of feed, the milk giving the largest display of cream often gave the least butter product, and the reverse. As far as we could judge, the character of the cream varies quite as much as the milk does in its original condition. In proof of this, we submit the following tabular statement, in which the average yield of butter and fat of all the different cream per cents obtained in the entire experiment is given in horizontal columns:

Table No. 3.

Cream, per cents	8.	9.	10.	11.	12.	13.	14.
Butter, per cent.	4.45	4.86	4.42	4.03	4.20	4.21	5.11
Fat, per cent. by test . . .	4.24	4.28	4.83	4.74	5.06	4.75	5.29
Theoretical fat, in proportion to cream	4.77	5.30	5.83	6.36	6.89	7.42

It seems scarcely necessary to add anything in the way of comment to the plain facts of the table. We see here that milk

showing eight per cent. of cream gives a larger yield of butter than is obtained from milk giving 10, 11, 12 or even 13 per cent. of cream; and while the column of fat per cents. shows a slight increase as the amount of cream increases, this gain comes far short of what it should be to keep pace with the increased amount of cream. This is seen at a glance in the column of 'Theoretical Fat,' where is given the calculated amount of fat for each per cent. of cream, taking as the basis of comparison the fat yielded by the least per cent. of cream (8). These facts are, if possible, brought out more strikingly in particular cases exhibited in the table giving the daily record of the experiment, where the neutralizing effect of the group averages is not seen. The truth is, that the man who buys the milk of a large number of herds, good, bad and indifferent, paying for it by the gauges of cream which it yields, is probably not greatly the loser or gainer thereby. Experience has taught him the amount of butter he has reason to expect from the composite cream; but the loss to patrons, especially those whose herds have been bred up in dairy lines, must often be very great in the averaging process. The farmer whose Jerseys, as in the case of our 'Pansy,' gave $9\frac{1}{2}$ to 10 per cent. of cream, yielding nearly five per cent. of butter, must, if all patrons are paid alike, contribute in the course of a year a very pretty sum towards the support of his neighbor's herd of scrubs, which, like our 'White' and 'Ruby,' gave nearly 11 per cent. of cream and only $3\frac{3}{4}$ per cent. of butter."

CREAMING QUALITY AND OIL TESTS.

The objection is frequently advanced to all forms of butter-fat or "oil" tests for milk, that they show the total amount of fat present instead of that obtainable in the cream by setting, and that therefore they cannot correctly measure the butter value of milk, or even the relative butter values of two or more milks, because of the varying "creaming quality" of milk from different breeds and different cows. That there is some force in this objection cannot be denied, but that there is force enough in it to throw such milk tests out of the category of practical and useful aids to the dairyman and breeder cannot be admitted. Dairymen and breeders themselves do not admit it, as is testified by the drift of a great number of letters coming to us constantly from these classes.

They probably reason it out in this way, which I believe to be correct: Admitting that by difference in "creaming quality" one might sometimes be misled regarding the relative butter capacity of two cows, in cases where the two show nearly the same total amount of fat, *were one to rely upon the test for total fat alone*, it nevertheless is not only possible but easy to escape being misled, by proceeding as follows in such doubtful cases: Set small portions of the two milks under the same (and the best possible) conditions for creaming; skim, and then test the skim milks for their content of butter-fat. This will tell how much fat was taken off in the cream, and the bug-bear of "creaming quality" will be vanquished! Too much work, is it said? Probably too much for some, but not too much for those in earnest for the facts. And even if this course were followed with every cow of the herd—a proceeding by no means necessary—the work would be trifling compared with that of setting the whole of each cow's milk by itself, skimming, ripening and churning separately.

As regards the practical utility of testing individual cows, evidence from the experience of practical men is fast accumulating, if we may judge from the columns of the agricultural papers. The following comes under my eye in *Hoard's Dairyman* as I write—a sample of the experiences which are being reported:

"Col. F. D. Curtis said that by testing his cows last summer he found that one, which he had regarded very highly, gave milk of such a poor quality that it required twenty-nine pounds of it to make a pound of butter. His cows varied in the amount of milk required for a pound of butter from 13 7-10 to 29 pounds. He said he should dispose of several that he should have regarded as good but for this test."

Concerning the reliability of conclusions as to the butter capacity of individual cows, *based upon tests of the milk*, the following experience of a Wisconsin man, (communicated by private letter), will be of interest:

"Having tested twenty-nine cows six times the past year by Short's method, and on adding up pounds of butter according to test, and pounds made by churn the former overran only twenty-five pounds on 4351 pounds. So I think my individual estimates nearly correct.

II. The Milk Test—

The above considerations led me to undertake the invention of a dairy test, on the "butter-fat" principle, which should meet this long felt want among milk producers. After some preliminary experiments the plan of attack which seemed most promising was to find some solvent which would completely dissolve all the milk constituents excepting the fat, without sensibly destroying or decomposing the latter. After some weeks of work I was gratified to feel that I had not only found such a solvent but had also succeeded in devising an apparatus for the effective application of the same.

This was in April or May, 1889. Since then the development of the process has consisted merely in improvement in details, not in any change in principle; therefore the first public announcement and description of the method, which appeared in the "Homestead" (Des Moines, Iowa), of June 14th 1889, is still correct except in minor details, and the following extract is taken from it. It was written by the editor, Henry Wallace, the facts concerning the method being furnished by myself.

FROM "THE HOMESTEAD" JUNE 14, 1889.

"Prof. G. E. Patrick, of the Iowa Experiment Station, has been for some time past engaged in testing the cows on the college farm. He found an astonishing variation in the amount of fat in the milk of the different cows, varying from two to seven per cent. This led him to a series of experiments for the purpose of discovering a more practical method of determining the amount of fat than as yet devised.

During a recent visit to the Station we became greatly interested in his newly discovered method, and after witnessing the process and comparing the results of a long series of experiments with the results obtained by the tedious but almost absolutely accurate "gravimetric" method, we are convinced that Prof. Patrick has furnished the farmer and dairyman with a test that is at once inexpensive, practicable and accurate, and that can be used on any farm and by any farmer that can take care of cows, meeting the requirements of efficiency, cheapness, rapidity and ease of execution more fully than any yet proposed.

The principle, or plan upon which it works, is entirely new, and

yet very simple. It is to dissolve the casein and albumen of the milk, by means of chemicals and heat, and to allow the melted fat to rise and collect in a narrow tube, where its volume can be read with accuracy. The chemicals employed must of course be such as will not destroy or decompose any of the fat, and still make a perfect solution of the other ingredients of the milk. Such a solvent Prof. Patrick has found in a mixture of strong acetic acid, (80 per cent. will answer)* oil of vitrol and hydrochloric acid (concentrated) in about the proportions of 9, 5 and 2, by volume.

The operation is conducted in a glass tube about $\frac{3}{4}$ of an inch in diameter and 12 inches long, closed at one end and made narrow for about three inches near the middle, where the proportion of fat is to be read. A measured volume of milk—an "assay volume" Prof. Patrick calls it, that is 10.8 cc.†—is poured into the tube; enough of the acid mixture is added (14 to 16 cc.) to bring the volume to a certain point in the tube, and the contents are mixed by shaking; the tube is set upright on a "sand bath" (a flat dish containing sand), which is placed on a hot stove or over some other source of heat. A dozen, or any number of tests can be made at once. The mixtures in the tubes are brought to a boil, (bits of pumice stone in the tubes make them boil evenly), and boiled well for ten minutes, then very gently for ten minutes more; by this time all of the milk excepting the fat will be entirely dissolved and the fat will float in a clear, oily layer on the surface.

The sand bath and tubes are now removed from the heat, and as the liquid cools, the oily fat sinks into the narrow part of the tube. For the farmer's purpose, where great accuracy is not required, the volume of the fat may be read at once, but if greater accuracy is desired the tubes may be set into a pail of water at a temperature of 140° F. for ten minutes, and the reading taken at that temperature. The reading is done by a small graduated scale, on wood, held against the tube.

The results of this method have been carefully compared with those of the gravimetric method, the most accurate method known to chemists, and have always been found in substantial agreement

*Ninety per cent. strength for the acetic acid is the only strength now used or recommended.

†Recently reduced to 10.4 cc. See page 95.

with the latter. The following figures are fair samples of the many which have been obtained at the Station laboratory:

(a) *On Whole Milk.*

<i>By Gravimetric Method.</i>	<i>By New Method.</i>
	{ 3.35 per cent.
	{ 3.42 "
3.33 per cent.	{ 3.33 "
	{ 3.35 "
	{ 3.40 "
	{ 3.31 "

(b) *On Whole Milk to Which Cream was Added.*

<i>By Gravimetric Method.</i>	<i>By New Method.</i>
	{ 9.57 per cent.
	{ 9.40 "
9.41 per cent.	{ 9.35 "
	{ 9.35 "
	{ 9.51 "

(c) *On Skimmed Milk.*

<i>By Gravimetric Method.</i>	<i>By New Method.</i>
	{ 1.02 per cent.
.92 per cent.	{ 1.02 "

A Sample Thrice Skimmed Gave:

<i>By Gravimetric Method.</i>	<i>By New Method.</i>
	{ .40 per cent.
.42 per cent.	{ .39 "

But few experiments have been made as yet with cream, but the results so far have been entirely satisfactory."

EARLY MODIFICATIONS.

Even at the time the above was written certain minor improvements were being tried which were adopted before the test was given to the public in material form. These were:

1. Instead of depending upon the subsidence and contraction of the liquid to lower the fat into the neck of the tube, it was found more convenient and much quicker to lower it by one of the mechanical devices described further on.
2. Having the graduated scale on the neck of the tube itself (etched), instead of on a rule or hand scale, proved to be a convenience more than sufficient to balance the small added expense.

A LATER MODIFICATION.

After some months' experience a strength of 90 per cent. for the acetic acid for making "acid mixture" was fixed upon as the

best, and the only strength to be used thereafter. Up to that time two qualities of acid mixture had been sent out, one made from 80 the other from 90 per cent. acetic; but the difference in cost was found to be too slight to make it any object to the consumer to use the cheaper quality. The latter is slower in action, but works fairly well on fresh samples of milk. Now, only the best quality is sent out (that made from 90 per cent acetic), and only that quality is recommended for use.

THE TUBES

used in the test are made after two different patterns, shown in Figs. 1 and 2.

Fig. 1 shows the form of which most have thus far been made. Its lower part or body, with an outside diameter of about 21 millimeters has a capacity of 20 to 21 cubic centimeters, and at two-thirds its length from the bottom is provided with a very small lateral orifice—1 to $1\frac{1}{2}$ mm. wide—at the point of a small elevation or spur; the neck has a caliber of $4\frac{1}{2}$ to 5 millimeters, is 6 to $6\frac{1}{2}$ centimeters long, and is carefully graduated by exact measurement of volume (or *should be*) so as to include exactly 1.000 cubic centimeter between 0 and 8, and .025 cc. in each of the 40 divisions into which the intervening space is divided. Every five divisions then measure together .125 cc., and every fifth line is marked with a numeral, from 0 to 8 (the figure shows these no higher than 7).

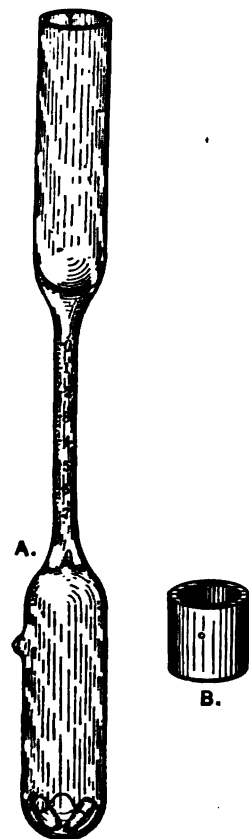


FIG 1.

The part of the tube above the neck is $14\frac{1}{2}$ cm. long—the figure shows it too short—and of 16 to 17 mm. caliber (inside).

B is a circular rubber band—a section of tubing—with a perforation which, when the rubber is slipped into place on the tube, must be just to one side of the orifice in the latter which is thereby tightly closed.

With a long stout pin used as a lever through the hole in the rubber it is easy to withdraw as much as may be desired of the contents of the tube, and thereby lower the fat into the graduated neck.

As a matter of fact the rubber band, which unsupported would soon lose elasticity and effectiveness, is supported and made to do efficient service for a long time by a copper band or ring (not shown in the figure), of such shape as in no wise to hinder the withdrawal of the liquid.

Lastly but not least in importance, the body of the tube contains a couple of pumice stones (or similar material) to promote regularity in boiling; and it is essential that at least one of them be sufficiently dense, or be made so by platinum wire, to remain at the bottom of the tube while the contents are boiling.

The other style of tube, shown in a dismembered condition in Fig. 2, has the advantage that the surface of the fat-column can always be brought to the zero mark, and the reading thus facilitated. It consists of the two glass parts A and C, and a thick rubber connecting-tube B. The latter is wired firmly to A, but allows the graduated neck (of C) to be moved up and down inside it, with moderate friction.

During boiling the neck is kept close down to A, but when the time for lowering the fat arrives it is drawn up until its lower end is but little below the small hole in the rubber B, and through this hole the liquid is easily withdrawn by the aid of a long stout pin. Should the surface of the fat, in lowering, happen to be brought a little below the zero mark, or should it fall below by reduction of temperature, its position can at once be readjusted to that mark by pressing the neck a little lower into the rubber B.

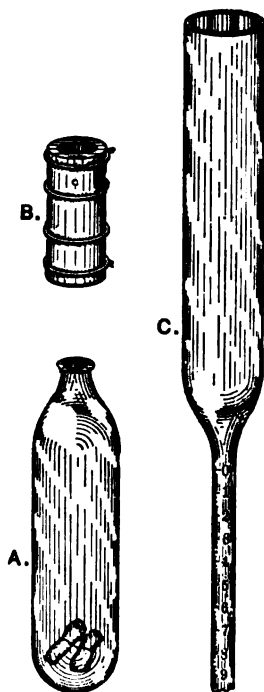


FIG. 2.

The same remarks about the pumice stones apply to this as to the style of tube first described (Fig. 1).

Which of these two styles of tube will on the whole give most satisfaction cannot be told until those of style No. 2 (Fig. 2) have been longer in practical use than at present.

The graduations are the same for both styles; the numerals thereon mean per centages by weight—that is, pounds of butter-fat per hundred pounds of milk.

OTHER APPARATUS.

The milk tubes above described, of which any number from one to a dozen may be used at once, stand upright on a "sand-bath"—a shallow copper pan holding sand—and are supported in that position by a zinc rack which, when removed from the sand-bath, carries the tubes with it. With sets of more than a half dozen tubes an extra rack is supplied, to be set in a pail of water at 140° Fahr. (See below.) With sets of six or less this extra rack is not needed.

[A single tube can be worked very well on an ordinary kitchen stove, with a tripod support in place of the large rack just mentioned, by letting a small pile of ashes placed on the hottest part of the stove serve as a sand-bath. Such an arrangement would be useful to consumers and others who desire to make only an occasional test of the quality of milk.]

Besides the above, the only articles required are,

A pipette for measuring the milk. (See below.)

A long stout pin for lowering the fat.

A Tube-Brush for cleaning tubes, and

A bottle of "Acid Mixture."

THE PIPETTE.

The capacity of the pipette for measuring the milk charges, in order that one cc. of average butter-fat measured at 140° F. should constitute *by weight* exactly 8 per cent. of the milk taken—as required by the scale on the tubes—was first determined by calculation, from the following data :

(1.) The average sp. gr. of milk, = 1.032.

(2.) The average sp. gr. of butter-fat at 100° Fahr. (at which

temp. many determinations have been made) = .9045 — water at 60° F. being unity.

(3.) The coefficient of expansion of butter-fat, per degree Fahr. = about .41 per 1000.

These data give a sp. gr. of .8899 as the average for butter-fat at 140° F. (water at 60° F. = 1); and further calculation from this gives 10.77 cc.—practically 10.8 cc.,—as the volume of milk required for a charge—the *assay volume* as I have ventured to call it.

This theoretical charge proved fairly satisfactory in practice, and although the tendency to somewhat high results was observed long ago, a change did not seem necessary until very recently, when, in consequence of a certain new improvement in the method making it possible to get quicker, "cleaner" and usually a trifle higher results, it became apparent that the *assay volume* must be reduced, as stated below.

RECENT IMPROVEMENT—CHANGE IN THE ASSAY VOLUME.

The improvement referred to is in the use of an alkaline sulphate — sodium sulphate because it is the cheapest — to assist the acid mixture in dissolving the non-fatty parts of the milk. Those who have used the method as originally described, know that there was often left undissolved, especially in testing old samples of milk, a small amount of gelatinous scum or curd adhering to the tube when the fat was lowered. This scum, besides containing a little fat not yet liberated, so to speak, is inclined to retain by adhesion small portions of the clarified fat, and thus to cause slightly lower results than would be obtained were the last traces of scum or curd entirely dissolved. Moreover, as the amount of undissolved scum varied with different milks, being greater as the age of a sample increased, the results were liable to vary accordingly, within narrow limits.

For these reasons I sought to get rid of the troublesome scum residues, and on Dec. 25, 1889, made the discovery that the addition of an alkaline sulphate (or bisulphate) to the acid mixture or to the charge in the tube during boiling — especially during the second boiling or "clarification" — causes the complete and speedy solution of the scum and hereby greatly hastens the clarification of the fat, without in any way affecting the latter except

to enable it to drain into the graduated neck practically without any loss by adhesion.

It is found best to apply the alkaline sulphate in both the ways just mentioned, viz: (1) in all cases by having it in solution in the acid mixture, and (2) when further treatment is needed to expedite clarification, by sprinkling the dry salt in the form of a *very fine powder* upon the layer of fat in the tube, while the contents are being boiled for clarification.

The alkaline sulphate which has been used in nearly all the work is the sulphate of soda, and as that salt is obtainable at any drug store it is adopted in the formulæ and directions, given below.

The acid mixture should be *saturated* with the salt—that is, be made to dissolve all it will.

Change of Assay Volume.—Time has not allowed of making a great number of tests in comparison with the gravimetric method since the above described improvement was made, but enough has been done to show that the *assay volume* must now be reduced by about 4 or 5 per cent. (on itself,) that is, *to about 10.4 or 10.3 cc.**

Some of the results point to the latter as the preferable figure; but in a method of this kind too low results are most to be avoided, therefore I adopt 10.4 cc. as the figure for the *assay volume* for the improved process until further experiment shall either verify it or indicate a better. Many tests in comparison with the gravimetric method will be required to determine surely whether this exact figure to the tenth of a cc. is the very best; but I am now entirely certain it is nearly enough correct to answer all practical purposes.

THE ACID MIXTURE.

Two formulæ for acid mixtures have been fixed upon as being about equally efficient upon samples of fresh milk! one of them, however—No. 1—possesses the merit of not developing any turbidity whatever even after much longer boiling than the process calls for; while the other—No. 2—is better adapted for work upon old milks, which as a rule are more difficult to dissolve com-

*This reduction is necessitated in part by the fact that I recently discovered the standard burette which is used for testing the milk tubes—and which I had with too much confidence relied upon without verifying, because costly and furnished as *absolutely correct* by a maker of high repute—to be too large by nearly 2 per cent. (on itself.) It is a matter of regret, and some mortification, that this error was not detected earlier; but fortunately, it was too small an error to occasion any real harm.

pletely than fresh samples. Thus No. 2 behaves like a "stronger" acid (although chemically it is not as "strong" or concentrated as No. 1.) and therefore *for general use* is the better of the two.

FORMULÆ.

No. 1.

Pure Acetic Acid of 90 per cent. strength	By Measure. 9 volumes.
Commercial Oil of Vitriol, sp. gr. 1.83	5 "

Mix, cool thoroughly, then add—

Hydrochloric Acid, Chem. Pure, sp. gr. 1.19	1 volume.
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Finally, saturate the liquid with sulphate of soda, that is, dissolve in it as much of the powdered salt as possible by shaking or stirring, and have an excess undissolved at the bottom after settling. The crystallized form (Glauber's salt) answers here.

Bottle immediately in glass-stoppered bottle; or, if such is not to be had, *cork tightly* in ordinary bottle, and keep it in a cool place, to prevent loss of hydrochloric acid gas.

No. 2.

Pure Acetic Acid of 90 per cent. strength	By Measure. 9 volumes.
Commercial Oil of Vitriol, sp. gr. 1.83	5 "

Mix, cool thoroughly, then add—

Hydrochloric Acid, Chem. Pure, sp. gr. 1.19	2 volumes.
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Finally saturate with sulphate of soda, bottle, and store in same way as for No. 1.

The charge of acid mixture to be used with an *assay volume* of milk in making a test is about 14 cc.—anywhere from 13 to 15 cc. answers well; therefore, it need not be measured out with more accuracy than can be done by pouring into the milk tube to a certain level, viz., $\frac{3}{4}$ inch to 1 inch above the top of the neck.

SULPHATE OF SODA

for sprinkling into tubes during clarifying. The proper form of the salt for this purpose is the "effloresced" salt. It is prepared by powdering common "Epsom Salt" as finely as possible in a mortar (iron or earthen), and then exposing in a thin layer to the air for a few days, to allow the "water of crystallization" to escape and the crystals to fall to a fine, impalpable powder; or

better, by drying the powdered salt at a gentle heat. The finer and dryer it is the better.

Any druggist will powder the crystallized salt; the purchaser can with very little trouble do the rest. A half pound will last a long time.

THE PROCESS.

Following are the directions for executing the test as modified by improvements to date. They are given in much detail, that the operator may not be without guidance at any point or in any emergency.

DIRECTIONS.

CHARGING THE TUBES.

Measure the *assay volume*—10.4 cc.—of milk into a tube by means of the pipette. To do this, fill the latter exactly to the mark by suction and the use of the forefinger, and transfer completely to the tube by blowing out the last drops. Do not run the milk in fast enough to choke up the neck of the tube.

Now pour in acid mixture (in a small stream, from small acid bottle) to within an inch or less of the neck—leaving room to allow mixing the contents; shake vigorously, to thoroughly mix the acid and milk, add acid mixture again up to three-quarters of an inch or an inch above the top of the neck, wipe the outside of tube dry and place it in the rack on sand bath.

The sand bath should contain sand free from gravel, to depth of about half an inch—a little more if a very hot fire is to be used.

DISSOLVING THE CURD AND RAISING THE FAT.

When all the tubes, or as many as you wish to use, are charged and in place on the sand bath, set the latter over a brisk fire in the kitchen stove—with stove lid off—or directly on the flame of a gasoline stove, not turned too high. Bring contents of tubes to a boil, and boil rather briskly, but not violently, for 4 to 6 minutes;* by this time the froth, which at first forms, will have disappeared, and the curd of the milk will be dissolved.

[If any tubes get the start of the rest, either in time or rapidity of boiling, they can be checked by raising them slightly in the

*If Acid Mixture No. 2 is used, four minutes are sufficient.

sand ; and on the other hand, if any are inclined to lag, they may be hastened by pressing a little deeper into the sand.]

Now set the sand bath to the back of the stove, or remove it entirely, in order to stop the boiling for 2 or 3 minutes, and allow the fat to rise to the surface. Lifting the tubes from the sand for a moment (all together, by means of the movable rack) will greatly hasten this result ; but they must not be kept long off the sand.

CLARIFICATION OF THE FAT.

As soon as the fat has risen, set the sand bath again over a heat sufficient to boil the contents of the tubes gently, so as to move the fat layer up and down, and even to mix it with the *surface portion only* of the acid liquid. This gentle boiling, with the motion and mixing of the fat layer, clarifies the latter from inclosed impurities. If the clarification is not *complete and perfect* after five minutes of this treatment (or 3 if time is precious), sprinkle upon the fat layer, *while it is being gently agitated, and mixed with the acid liquid*, as described, a little "effloresced" sulphate of soda. If *perfect*, clarification does not ensue almost immediately, repeat the dose, under the same conditions.

Under this treatment the time required for complete clarification, with a fresh milk, rarely exceeds eight minutes, and usually five suffice.

Now remove the entire apparatus from the stove.

TEMPERATURE FOR MEASURING THE FAT.

TIME OF IMMERSION IN BATH.

For many purposes, where great accuracy is not demanded, it suffices to at once lower the fat into the neck of the tubes and measure ; but where greater accuracy is desired the tubes should be set (all at once, by the movable rack) into a pail of water kept at about 140° F., and left there for 7 or 8 minutes before lowering. This brings the fat to the correct temperature, also makes it still clearer, and renders exact measurement easier. After lowering the fat, the tubes should be replaced in the water for a few minutes to allow the fat to drain down completely before reading ; the readings may then be taken after an immersion of 10 to 15

minutes, all told. Results thus obtained will be sufficiently accurate for all practical purposes.

But if the most exact results attainable by the method are desired, the immersion must be prolonged to a total of 30 minutes.

LOWERING THE FAT.

Lower the fat into the neck of the tube by using a stout pin (which accompanies the tubes) as a lever, through the hole in rubber band, to raise the latter from the orifice in the tube lying just under the circular hole in the copper ring, and allow the acid liquid to escape. Return to the water bath for the longer or shorter time directed above.

MEASURING THE FAT.

Both the upper and lower surfaces of the fat should be perfectly clean and distinct when the measuring is done. Should either be obscured by small bubbles and adhering brown liquid, these can be readily removed by inserting in their midst a slender twig of broom corn, twirling it rapidly between thumb and finger, and then returning the tube to the warm water to settle for a few minutes. [As the broom-corn twig is withdrawn allow the adhering trace of fat to drain off upon the glass just above the column of fat.]

Measure the fat from the extreme upper to its extreme lower surface; pay no attention to the meniscus—the dark crescent-shaped appearance just below the upper surface.

The numbers on the graduations indicate percentages of butter fat, by weight—that is, pounds of butter fat per 100 lbs. of milk. Each small division means .2 of 1 per cent. (that is, one-fifth of a pound per 100 lbs. of milk), and it is easy to read to one-half, and with practice even to one-fourth of a division.

In ungraduated tubes the fat is measured with a small millimeter scale. Special directions for this will accompany such tubes.

EMPTYING AND CLEANING THE TUBES.

While they are still warm, pour warm water into each tube to fill it and float the fat to its very mouth. If the fat lags in rising, a broom corn twig inserted will bring it up at once. When it is

all at the top, throw it out of the tube with a quick motion, then pour out the liquid, turning the tube as you pour. In this way the fat is entirely removed, and the tube is cleaned by the acid liquid itself; it needs only rinsing twice with warm water to be ready for use again. Occasionally, cleanse with the brush.

N. B.—For dissolving *old* samples of milk, always use Acid Mixture No. 2; but with this acid avoid too long boiling in dissolving the curd.

With *fresh* milks, Acid Mixture No. 1 is as efficient as No. 2, and with it considerable longer boiling than called for by rule, does no harm.

With exercise of care, however, and *for general use*, Acid Mixture No. 2 is preferable.

Keep the Acid Mixture in a glass-stoppered bottle, or if not, then a bottle *tightly corked*, and in as cool a place as possible.

A gasoline stove serves fairly well as a source of heat, when not convenient to use a common cook stove.

(The above is a copy of the directions sent out with the apparatus.)

SPECIAL PRECAUTIONS.

1. In charging the tubes, empty the pipette *completely* of milk, by draining for a few seconds and blowing through it.

2. Bring the contents of the tubes to a boil as quickly as possible. If Acid Mixture No. 2 is used boil briskly only four minutes; much longer boiling is liable to make clarification more difficult.

3. After the first boiling is over and all boiling has ceased, allow sufficient time (two to three minutes usually) for *all* the fat to rise to surface before commencing clarification. Observation through the neck of the tube toward the light of a window will tell when all has risen.

4. In clarifying, boil only briskly enough to agitate the fat and mix it with the *surface* portion of the acid liquid, but *not briskly enough* to carry any fat down again into lower part of tube.

5. In lowering the fat, rest the tube on some support; do not try to hold it in mid-air.

6. If the plan of "*hot reading*" be adopted—i. e. reading as

soon as clarification is done, without setting into water—make sure before reading that all the fat has risen to the surface.

REMARKS ON THE PROCESS.

The Hot Water Treatment.—Its Omission.—If standing of the tubes in water at 140° Fahr. be omitted and the fat be read while *hot*, as soon as clarified, results will be higher by .15 to .25 per cent. than if read after a half hour's immersion in the water; but the saving in time is so great by the former course that it is the better one to pursue when *comparative* rather than *absolute* results are desired and when only a few tests are to be made at once. With more than half a dozen tubes on the sand bath however, the plan of *hot* reading is not practicable for a single operator, and in such cases it is better to follow the plan of immersion—not necessarily for thirty minutes, but for a sufficient time to allow the temperature of all to be fully reduced to that of the water (140° Fahr.), namely, about ten minutes. After that time the volume of the fat diminishes but little; the reading after thirty minutes being commonly only about .05 per cent. lower, on an average milk, than after ten minutes in the water; therefore for practical purposes an immersion of ten minutes before reading is long enough.

Removal of Tubes to Hot Water—Extra Rack.—With ten or a dozen tubes on the sand bath at once it is not easy to have them all ready for removal to the hot water at exactly the same time, therefore when so many are being worked, instead of attempting to remove them all together by means of the rack it is preferable to remove them one at a time, as soon as "done," to a second rack immersed in the hot water. For this purpose an extra rack is provided with sets of more than six tubes.

Time Required for Making Tests.—By the "short cut" plan of reading the fat *hot* (i. e. omitting the immersion in water), the testing of a single sample consumes about twenty minutes all told, and a half dozen can easily be done in a half hour after the tubes are charged.

By the regular plan of immersion in water, for ten minutes ordinarily or for thirty minutes if the most accurate results attainable by the process are aimed at, more time proportionately is consumed.

SOURCES OF ERROR.

Chemical.—The only danger of error from a chemical source that I have discovered, is in failing to completely dissolve the non-fatty parts of the milk; and on reasonably fresh samples this danger is practically nothing. Even after becoming sour and curdled perfect solution is in general easily effected; the longer it remains curdled, however, the less easily does it dissolve.

The only kind of milk which, in my experience, has presented real difficulty in dissolving, and which therefore could not be satisfactorily tested has been *buttermilk*. With some samples of this the method failed completely, and with none has it been really successful, yielding always a turbid solution—if solution it could be called—and a dirty, hardly readable layer of fat. Therefore I do not recommend the method as a test for buttermilk. It is true this experience was had before the recent improvement in the method (use of sulphate of soda, see ante), and time has not since allowed a renewal of the buttermilk trials. This will be done at an early day, but past results do not encourage the hope of much success.

Fortunately, whatever be the sample operated upon, whether sweet milk, skim milk or buttermilk, the operator can always tell whether the method is working successfully or not: *a clear (nearly or quite transparent) solution of the milk, with a clear fat layer free from curd and scum*, is a sure proof of the successful working of the test.

Mechanical: Graduation of the Tubes—The chief source of error to which the method is liable—and in testing fresh milks, practically the only one to be feared—is in the graduation of the neck of the tubes, where the fat is read.

It would seem in theory that great exactness and uniformity might be reasonably expected in the graduation of these tubes, and it is in fact possible for such work to be done with almost absolute correctness; nevertheless it is in practice almost impossible to get any considerable number of them made uniformly in that careful manner, at least without great and unusual expense. The majority will be somewhat near right—near enough for most purposes perhaps—but human nature is such that *unless the makers*

know that their work is to be carefully tested, condemned and returned if found faulty, a considerable number will be much too far from correctness to bear out the truth of the adage "figures will not lie." In short it is a known fact, based upon experience, that unless the greatest precautions are taken *without ceasing* to secure accuracy in the graduation of such instruments, they will surely be made more or less inaccurate—more rather than less as time goes on—until confidence will justly be lost in all the instruments, good and bad; and the method, however good in itself it may have been, will have lost its reputation.

This is not theory, but fact—in evidence whereof I could cite the experience of a number of persons, but will only quote from Bulletin No. 16 of the Vermont Experiment Station (July, 1889, page 3), in which the Director, in speaking of another method of testing milk which I myself know to be an excellent one, says:

"It does seem necessary, however, to call the attention of those who intend to make use of this method, to the liability of getting tubes which are not properly made and hence worse than useless. We have bought sets of tubes from three large firms whose names are each considered a guarantee of good work and only one of the firms has sent us reliable tubes. This was a wholly unexpected danger and one that unless immediately avoided must quickly bring this—(calling it by name) method into disrepute. There is reason to believe that each of the firms that sent out incorrect tubes have since made a new supply of correct ones, but it is probable that there are already in the hands of farmers and creamery-men a large number of worthless tubes that it is desirable should be found out and thrown away. This Station will test free of charge any tubes that are sent in by express prepaid and will return the same as soon as tested."

WHAT THE IOWA STATION WILL DO.

We wish to guard the "Iowa Station Milk Test" from the fate pictured in the paragraph just quoted, and propose to do it—so far as we have the power to do it at all—on the principle that "an ounce of prevention is worth a pound of cure." In other words the Station will protect the interests of the public, as well as the reputation of the new milk test, by testing the tubes *before* they

go out to the public and *before* any mischief is done instead of *after*. In fact this is already being done and has been done for months past, as many readers of this bulletin are already aware.

It is done in this way: The Station, having no right to go into business in any way, even for the benefit of the agricultural classes, secured the co-operation of J. F. McLain, of Ames, Iowa, doing business within two miles of the Station, so that the two can work together easily. He manufactures the metallic parts of the apparatus and does the "business." The tubes are made under special instructions, either in the East or in Germany. On arrival at Ames they are sent in bulk *direct to the Experiment Station* where they are carefully tested as to accuracy by measurement of each one separately with mercury and a standard burette, checked by an analytical balance; those found to be inaccurate (as defined below) are marked indelibly with the word "incorrect" (by means of hydrofluoric acid) before returning to the makers; those found to be absolutely or substantially correct are *kept at the Station* and delivered to Mr. McLain *only in sets as ordered by purchasers*, each set being accompanied by a *certificate of accuracy* from the Station Chemist, *stating also the number of tubes in the set*. In this way it can be positively affirmed that every milk tube sent out from Ames, if accompanied by certificate of accuracy from the Station Chemist, has been actually proved to be substantially accurate by measurement in the Station laboratory; and further, that those found to be "incorrect" will never, by accident or otherwise, be sold as correct.

WHAT ERROR IS ALLOWED?

The exact meaning attached to the terms "incorrect" and "substantially accurate" in the above statements may be known from the following rule, no departure from which is allowed for any reason whatsoever. No tube shall be passed as "correct," "substantially correct" or "substantially accurate," whose deviation from the standard burette is greater than three-tenths of one per cent. for the entire eight per cent. covered by the scale—that is, .15 per cent. on the four per cent. of fat in an average milk. Of course on most that are passed as correct the error, if there be any, lies considerably within these limits.

ASSORTING OF TUBES. COMPARATIVE ERRORS ELIMINATED.

After the tubes are tested, the "correct" ones are assorted into groups, each group comprising those of the same or very nearly the same deviation from the standard. Thus each set sent out consists of tubes *uniform in graduation* among themselves, so that the small absolute errors allowed within the prescribed limits *are for purposes of comparison eliminated*.

By the measures and methods above described, which will be strictly adhered to until official notice to the contrary is given, it is hoped to keep the standard of the "Iowa Station Milk Test" above reproach.

RESULTS.

Several scores of trials have been made of the "test" in comparison with the (Thomson-Adams) gravimetric method. To give all the results would require too much space; as good an idea of the character of the work done will be gained from the following selections, which are representative:

Date.	Sample.	Gravimetric.	The Iowa Station Test.
		Thomson's modification of Adams' Method.	By the original method, and old assay volume 10.8 cc.*
1889.			
Dec. 2	New milk.	4.27	{ 4.30 4.30 4.35 4.35 4.35 4.30 4.32—mean 4.32
Dec. 3	New milk, enriched with cream.	7.67	{ 7.70 7.85 7.80 7.75 7.80 7.82 —mean 7.79
Dec. 4	New milk.	4.50	{ 4.60 4.50 4.60 4.50 4.55 4.55 —mean 4.55
Nov. 30	New milk, extra rich.	7.06	{ 7.10 7.20 7.15 7.20 7.20 7.30 —mean 7.19
Nov. 29	Half skimmed milk.	1.43	{ 1.45 1.47 1.40 1.40 1.45 1.47 —mean 1.44
Dec. 7	Skimmed milk.	.55	.55 .60
June 4	Skimmed milk.	.92	1.02 1.02
June 5	Skimmed milk.	.42	.40 .39

*Correction for small errors in the tubes accounts for the apparently over-exact figures. The readings themselves were seldom taken closer than 5 in the second decimal place—i. e., .05 per cent.

Date.	Sample.	Gravimetric.	The Iowa Station Test.
1890.			By the improved method: use of sulphate of soda and new assay volume, 10.4 cc. Following are results of all the trials yet made.
Feb. 4	New milk.	3.90	{ 3.95 3.96
Feb. 5	New milk, enriched.	6.54	{ 6.65 6.72 6.68
Feb. 6	New milk.	3.91	{ 6.71 6.57 —mean 6.66
Feb. 7	New milk.	4.92	{ 3.96 3.97
Feb. 12	New milk.	4.10	{ 5.00 4.98 5.02 4.99
Feb. 18	New milk.	3.50	{ 5.04 4.98 4.92 5.02
Feb. 19	New milk.	4.22	{ —mean 4.99
Feb. 20	New-milk.	3.84	{ 4.13 4.18
			{ 3.51 3.55 3.58
			{ 3.51 —mean 3.53
			{ 4.22 4.25
			{ 3.87 3.92

CREAMS.

Tested by diluting with two or three volumes of water, as required by richness of sample, proceeding as usual and multiplying the result by three or four as required. It is often difficult to take a true sample of cream thus diluted, because of the tendency of the fat to rise; the error thus introduced, as well as the unavoidable errors of the process are in the results increased three or four times by the act of multiplying, therefore neither very accurate nor very concordant results can be expected in testing cream. The error seems liable to reach as high as .5 per cent. on average creams. Only three samples tested.

Date.	Sample.	Gravimetric.	Station Test. Improved Method.
1890.			
Feb. 5	Cream.	28.31	{ 28.00 27.97
Feb. 6	Cream, thin.	19.46	{ 28.43 28.20
Feb. 12	Cream, thin.	17.70	{ —mean 28.15
			{ 20.07 19.47
			{ 19.76 19.90
			{ —mean 19.80
			{ 17.30 17.22
			{ —mean 17.26

THE DETERMINATION OF MORPHINE.

Colorimetric Method for Estimating the Morphine Strength of Laudanum and other Preparations of Opium.—J. Hinsdale, Chem. News 62, 77. An official tincture of opium with assayed opium is made, the morphine strength of the tincture being known, and three dilutions of it with dilute alcohol are prepared as follows :

One	3	parts	tincture	and	1	part	dilute	alcohol.
"	2	"	"	"	2	"	"	"
"	1	"	"	"	3	"	"	"

12 cc. of the tincture and of the dilutions are put in vials, and to each 12 cc. of dilute alcohol is added, when the vials are well corked, and kept as standards, labeled Nos. 1, 2, 3 and 4, No. 1 being the dilute official tincture. 0.04 gm. potassium ferricyanide is dissolved in 500 cc. water, and 15 drops of liquor ferri-chloride are added. This mixture must be freshly prepared. 50 cc. clean glass tumblers are placed on a white surface, and one drop of the dilutions are delivered from a pipette into the glasses, commencing with No. 4, the weakest. (The pipette should be about 4 inches long, of $\frac{1}{4}$ inch glass and tubing, and should deliver drops of the dilutions weighing about 0.016 gm. or $\frac{1}{4}$ grain.) 5 cc. of the ferricyanide mixture is added, and in about one minute 15 or 20 cc. of water, and the shades of color are observed. The ferricyanide mixture is said to be so delicate a test that one drop mixed with a drop of water containing 0.000001 gm. of morphine will yield a blue color within a minute. To estimate the strength of vinous or aqueous compounds of opium, they must first be brought to about the same specific gravity as the standard dilutions, with alcohol, that the drops may be uniform in size.

A. H. W.

Recovery of Absorbed Morphine from the Urine, the Blood, and the Tissues.—Theodore G. Wormley, Chem. News 62, 65, 79, 99. ("The University Medical Magazine.") Amyl alcohol was examined, as a reagent applicable for the extraction and recovery of morphine, Kahlbaum's (density 0.811 at 20° C.) being used. This alcohol, which is almost wholly insoluble in water, will, however, take up or dissolve a limited quantity of water. If 100 volumes of the alcohol be agitated with 20 volumes of water, after

complete separation of the liquids, the aqueous liquid will be reduced to 11 volumes, and the alcoholic increased to 109 volumes, or 1 volume of water is taken up by 11.11 volumes of alcohol. On digesting an excess of finely powdered morphine with amyl alcohol, at the ordinary temperature, for some hours, frequently agitating, one part of morphine is dissolved by about 150 parts by weight of alcohol. Under the action of heat, one part of morphine is soluble in 50 parts of the hot liquid, and a hot saturated solution of this sort, after cooling and standing for an hour, will contain one part morphine in about 62 parts of the alcohol, after 20 hours, one part in about 82 parts of alcohol. The salts of morphine are extracted more or less from their aqueous solutions by amyl alcohol. The equivalent of 25 mgms. of pure morphine, in the form of a salt, was dissolved in 5 cc. of water, the solution was agitated with 25 cc. pure hot amyl alcohol, when the mixture was allowed to stand for 20 hours. The clear amyl alcohol then held in solution the following amounts of morphine :

	Amyl Alcohol. Extracted.	Aqueous Solution. Retained.
	Mgms.	Mgms.
Morphine as acetate	8.93	16.07
" " sulphate	4.20	20.80
" " hydrochloride	3.60	21.40

Under similar conditions, except that 25 cc. of the alcohol already saturated with water was employed, the following were the results :

	Amyl Alcohol. Extracted.	Aqueous Solution. Retained.
	Mgms.	Mgms.
Morphine as acetate	5.0	20.0
" " sulphate	2.8	22.2
" " hydrochloride	2.5	22.5

and the conclusion from these results is obvious. In the extraction of morphine in its free or uncombined state from the urine by amyl alcohol, the large proportion of urea taken up by the alcohol interferes with the results. On digesting an excess of finely powdered urea with hot amyl alcohol, and allowing the mixture to stand some hours, the liquid was found to still contain in solution one part of urea in 78.8 parts of the alcohol. Certain extractive matters of the urine which have a strong reducing action exert a

still greater interference, by tending to cause misleading results. When urea is taken up with the morphine, the mixture may be decomposed by heating in an air bath for a few hours at 135° C. without any appreciable loss of the morphine, but the presence of the decomposition products of the urea is almost as objectionable as the urea itself. Urea is freely soluble in water, while morphine being only slightly so; separation may be made thus in pure mixtures or when the morphine is in the crystalline condition; but when only minute quantities of the alkaloid are present, this method does not answer, since the morphine adheres so closely to the urea and coloring matter that they are largely dissolved together. In experiments with isobutyl alcohol (Schuchardt's), on treating an excess of morphine with the hot alcohol and allowing to stand sixteen hours, it was found that one part of morphine was held in solution by 110 parts, by weight, of alcohol, while under like conditions, one part of urea was dissolved in 49.8 parts by weight of the alcohol, proving that morphine is less soluble in isobutyl than in amyl alcohol, while, on the other hand, urea is more easily soluble in the former than in the latter. Interesting cases are recorded in the article of practical application of amyl alcohol for extraction in toxicological examinations for morphine.

A. H. W.

THE SEPARATION OF TIN AND ANTIMONY.

A weighed quantity of the finely powdered sample is fused in a nickel crucible with ten times its weight of a mixture of sodium carbonate and one part of borax. After fusion and solution in dilute hydrochloric acid, the liquid is poured into a flask, diluted to the mark, and a known quantity is pipetted into another flask and saturated with H_2S . The sulphides thus precipitated are filtered off and collected by means of a plug of cotton inserted in the neck of a funnel. After once washing, the cotton is removed, and placed in a beaker containing a strong solution of sodium hydroxide, which is kept at the boiling point for a few minutes. The tin and antimony sulphides are thus converted into soluble sodium sulpho-stannate and sulpho-antimoniate. After filtering the solution, the filtrate is divided into two portions and placed in flasks marked *A* and *B*.

To the flask *A*, oxalic acid in large excess is added, and the solution boiled until the antimony sulphide that remains presents an orange-red color. The precipitate is filtered off, decomposed in a porcelain crucible, and weighed as Sb_2O_3 . To the flask *B* an excess of HCl is added, and the reprecipitated sulphides are treated precisely the same as in the previous case, and weighed as oxides. The total amount of tin is found by deducting the weight of oxide obtained from *A* from that of the mixed oxides obtained from *B*, and calculating to metallic tin. A judicious use of borax in the commencement of the operation is essential to success. (H. N. Warren, Chem. News 62, 216.)

A. H. W.

DETECTION OF HOP SUBSTITUTES IN BEER.

The authors have found the following method to give the most satisfactory results. Other reagents, especially ferric acetate, have been found useful, but the results of these experiments are not ready for publication.

OUTLINE PROCESS FOR THE DETECTION OF BITTER PRINCIPLES IN BEER.				
1 liter of beer is evaporated to $\frac{1}{4}$ and precipitated boiling with neutral lead acetate; the liquid boiled for fifteen minutes and filtered hot. If any precipitate occur on cooling, the liquid is again filtered.				
PRECIPITATE contains <i>hop bitter</i> , <i>caramel bitter</i> , <i>ophelic acid</i> (from <i>chiretta</i>) phosphates, albuminous matters, etc., etc.	FILTRATE. The excess of lead is removed by passing sulphuretted hydrogen, and the filtered liquid concentrated to about 150 cc. and tasted. It is then slightly acidulated with dilute sulphuric acid, and shaken repeatedly with chloroform.			
	CHLOROFORM SOLUTION on evaporation leaves a bitter extract in the case of <i>gentian</i> , <i>calumba</i> , <i>quassia</i> , and <i>old hops</i> (only slightly or doubtfully bitter in the case of <i>chiretta</i>). The residue is dissolved in a little alcohol, hot water added, and the hot solution treated with ammoniacal basic lead acetate and filtered.		AQUEOUS LIQUID is shaken with ether.	
	PRECIPITATE contains <i>old hops</i> , <i>gentian</i> , and traces of <i>caramel</i> products. It is suspended in water, decomposed by sulphuretted hydrogen, and the solution agitated with chloroform.	FILTRATE is boiled to get rid of ammonia, and treated with a slight excess of sulphuric acid, filtered and tasted. If bitter, it is agitated with chloroform, and the residue examined for <i>calumba</i> and <i>quassia</i> .	PRECIPITATE is treated with water and decomposed by sulphuretted hydrogen. The filtered liquid is <i>bitter</i> in presence of <i>gentian</i> .	FILTRATE is treated with a slight excess of dilute sulphuric acid, filtered and tasted. A bitter taste indicates <i>calumba</i> or <i>chiretta</i> , which may be re-extracted with ether and further examined.
CHLOROFORM SOLUTION is examined by special tests for <i>gentian</i> and <i>old hop</i> bitter.	AQUEOUS SOLUTION contains traces of <i>caramel bitter</i> .		PRECIPITATE is treated with water and decomposed by sulphuretted hydrogen. The filtered liquid is <i>bitter</i> in presence of <i>gentian</i> .	
			FILTRATE is treated with a slight excess of dilute sulphuric acid, filtered and tasted. A bitter taste indicates <i>calumba</i> or <i>chiretta</i> , which may be re-extracted with ether and further examined.	
		AQUEOUS LIQUID , if still bitter, is rendered alkaline and shaken with ether-chloroform. A bitter extract may be due to <i>Berberine</i> (<i>calumba</i>) or <i>Strychnine</i> . The aqueous liquid, separated from the ether-chloroform may contain <i>Caramel bitter</i> or <i>Choline</i> (somewhat bitter).		

In conclusion, we may say that the best way to taste bitter principles is to place some of the solution on the back of the tongue with the aid of a small pipette. When there is sufficient material, some of the solution may be swallowed with advantage. But the anterior parts of the tongue are far less sensitive to bitter principles than the parts towards the uvula. (Allen & Chattaway, *The Analyst* 16, 181.)

S. C.

THE OILS AND FATS.

Examination of Oils, Fats and Allied Substances.—Thomas T. P. Bruce Warren, *Chem. News* 62, 27. The author divides the substances about which he writes into three classes, depending upon their behavior with sulphur chloride. The solid magma which some of them yield with this reagent may be (1) either totally soluble in carbon disulphide, or (2) only partially soluble, while (3) others simply act as solvents and undergo no change. Oils and fats obtained from animal sources, fish oils, and the concrete vegetable oils do not yield insoluble products, but are easily separated from the fluid vegetable oils, when a mixture of them is treated with sulphur chloride. Oils obtained from pine resins, and fluid vegetable oils when deprived of a portion of their glycerine, also give no insoluble products. By passing a rapid stream of oxygen or ozonized oxygen preferably, through a mixture of these oils, the more readily oxidized oil can be separated from those not so readily acted upon. The fatty acids of these oils do not form insoluble compounds and are recognized by yielding dark colored products. Olive oil adulterated with cotton-seed and lard oil can be recognized in this way. The lard oil may be extracted from the solid magma by carbon disulphide. Another portion, after oxidation, and treatment with carbon disulphide, gives up both the lard oil and the fatty acids of the cotton-seed oil, while the insoluble magma will be very dark, owing to the difficulty of entirely removing the oxidized oil, but a moderately strong alkaline solution will more effectually remove it. Pure olive oil acted upon for some time with ozonized oxygen shows little or no absorption as indicated by the color of the insoluble product, whilst drying oils or the more readily oxidized oils, such as poppy oils, seed oil, walnut oil, linseed, rape, and cotton-seed oils, are readily

recognized. After ozonizing these oils, a reduced factor for iodine absorption is at once apparent, the extent or rapidity of oxidation being measured by the rate of diminution of iodine absorption. A "cold drawn" oil has a higher iodine absorption than when heat is used and when the oil has been extracted from the seeds by solvents, a still higher absorption is noticed, due in a great measure to oxidation. Cotton-seed oil, as such, is rarely used for adulterations, the olein or stearin both more or less impure being used. The viscosity of an oil before and after treatment with oxygen should be carefully noted. A drying oil is detected by an alteration in the iodine absorption and increased viscosity. In using Hubl's reagent for iodine absorption, a litre may be made, but as it rapidly changes, it should not be kept longer than a week or two. The solutions of mercuric chloride and iodine separately will keep fairly well, but mixed, will change every day. To obviate this difficulty, alcoholic solutions of the required strength are made and mixed as required. A blank test on the same amount of Hubl chloroform should be made under the same conditions as for the examination of the sample. The reaction is allowed to go on in a dark cupboard, which is supplied with a registering thermometer. An accurately stopped yellow tinted 6 oz. flask is used, the upper part being enlarged to admit of being luted with a little potassium iodide solution to catch any iodine which may escape, while the close fitting glass cap covers the stopper and lute. The reaction is allowed to proceed for twenty to twenty-four hours, as after eighteen hours no appreciable change occurs. Volatile liquids are weighed in a stoppered flask or measured from an accurate pipette. Experiments demonstrated quite a difference in the coefficient of expansion of different oils, although it is generally assumed that all oils have the same coefficient of expansion.

A. H. W.

Examination of Fats, Oils, and Allied Substances.—Thomas T. P. Bruce Warren, Chem. News 62, 51. Sulphur chloride exerts a selective action on a mixture of two oils, each of which yields an insoluble product with the reagent, so that one of the oils is, relatively, more affected than the other, and the author thinks it possible to make a fractional separation by adjusting the amount of chloride. Castor oil yields a small proportion of soluble matter

and is so energetic in its action, that the chloride must be diluted to moderate its effect. Rape oil as an adulterant only slightly modifies the action, and when the magma is treated with carbon disulphide, the soluble portion will be richer in rape oil products as the quantity of castor oil is increased. When the yellow chloride of sulphur acts upon the oil, the chlorine is evolved principally as HCl , while the sulphur at the same time unites with the dehydrogenized portion. An investigation of the action where oils do not yield insoluble products remains to be pursued. The total weight of the solid magma is to be carefully noted, but the subsequent treatment with solvents affords a far better clue to the nature of the substances under examination—5 gms pure lard gave 5.80 gms. solid matter, entirely soluble in CS_2 , with an iodine absorption of 52.60 per cent., whilst adulterated lard oils yielded insoluble products with CS_2 , as shown by the following table :

<i>Sulphur Chloride.</i>			<i>Iodine Absorption, per cent.</i>		
	Total Weight Magma.	Grams Soluble	Original Oil.	Extract from Magma.	Remarks.
Lard	5.80	5.80	52.6	47.40	Our rendering.
Lard Oil . . .	6.25	0.75	93.2	48.58	American.
"	6.19	0.48	89.9	52.06	English.
Cocoanut Oil .	5.14	5.14	. .	14.70	

The results for the cocoanut oil show the differences in weight between fats giving no insoluble products and adulterated oils containing an oil which gives an insoluble product. The iodine absorptions show that the oils or fats which yield no insoluble products are but little altered by sulphur chloride, whereas, a mixture of such an oil or fat gives a soluble portion entirely different in its iodine absorption and more closely approaching that of pure lard under similar treatment. An oil or fat not solidified by sulphur chloride gives an increase in weight very different from oils yielding insoluble products, and the removed portion gives an iodine absorption wholly unlike the original oils or mixtures. Lard oil as a lubricant, may be made up in one of two ways; animal fatty matter may be added to cotton-seed oil, or the stearin from cotton-seed oil may be in excess of what the oil naturally contains, and this may be added to animal fat. Refrigeration and pressure will enable us to recover the olein, however, and then the iodine absorption of the substance left on the filter as

well as of the olein will help to discover the fraud. Animal oils or fats will not blend very intimately with vegetable fluid oils. A mixture of cotton-seed oil and lard was saponified, the fatty acids separated, and reconverted into their corresponding glycerides and purified by recovery from CS_2 solution. When treated with chloride of sulphur this mixture showed no difference, the oil and the lard having recovered their own individuality from which case the deduction is made that a mixture of oils may be so completely altered by time, exposure, or other causes that identity of its original composition may be hopeless.

Estimation of Oils, Fats and Allied Substances.—Thomas T. P. Bruce, Warren Chem. News 62, 75 and 125. Poppy oil, which is said to be used largely for adulterating olive oil, was critically investigated, the results being tabulated below. 5 gms. were used in each case.

No. of Sample.	Sulphur Chloride.		Iodine Absorption.		Remarks.
	Magma.	Soluble.	Per cent. Original Oil.		
1	6.46	1.958	131.1		Four years old.
27	6.36	1.538	135.0		
74	6.08	2.382	92.4		Very old.
29	6.50	0.692	135.2		Glaucium flavum expressed.
50	6.55	0.629	139.1		
86	6.46	0.768	140.7		Glaucium flavum by CS_2 .

The iodine absorption shows the variation arising from oxidation. The weight of magma by sulphur chloride shows that the yield of soluble matter is increased as the total weight is reduced. Sample 74 gave a black pasty magma, and oils extracted by solvents yield less than those which are expressed, while blown oils (i. e. those thickened by oxidation) give less total magma than the same oils not blown. Experiments on rape and cotton oil revealed the following facts. The product from the thickened oils (which yield less magma than the same oils not thickened or oxidized,) is darker in proportion to the amount of oxidation, and from the consequent loss of glycerine there is a greater soluble extract. Cotton oil not thickened gives a very large proportion of soluble matter. Drying oils, as a general rule, give the greatest amount of total magma, which is for the same oil nearly proportional to the iodine absorption. Oils drawn by hot pressure have a low iodine absorption, due to the liability to oxidation in manu-

facturing them. Boiled linseed oil gives a dark pasty magma, similar to old poppy oil. For the iodine absorption, the Hubl reagent was prepared by dissolving 50 gms. pure resublimed iodine in alcohol (sp. gr. .795 at 60° F.) and making up to 500 cc. 60 gms. powdered mercuric chloride were dissolved in another portion of the same alcohol and filtered, and the alcohol washings of the filter kept to make up to 500 cc. The solutions were kept separately in a cool dark cupboard. Equal parts of the solutions were mixed together just before use and the reagent was standardized with sodium thiosulphate in the ordinary way. The oil, after digesting with the reagent and chloroform was emptied into a stout glass and the flask was rinsed out with 10 cc. of a ten per cent. solution of KI and 40 cc. of water, and afterwards with 100 cc. of water in two separate portions. During titration the whole was stirred with an ebonite rod to avoid scratching the glass. If mercuric iodide is precipitated on dilution, the KI should be added in crystals rather than in solution. Sulphur chloride was prepared by distilling the commercial yellow chloride and collecting the portion coming over at about 284° F., that coming over below this temperature being digested with an excess of sulphur and redistilled when required. The chloride thus prepared may be kept for some time with an equal volume of CS₂ in a clean well-stoppered bottle. The bulk of the chloride was kept in a bottle with a paraffined cork, and placed in a cool place. If two oils be mixed together, and we know the iodine absorption of each and of the mixture, the simple calculation will give us the proportion. For example, a mixture of olive oil and sesame oil is found to have an iodine absorption of 96.4 per cent. Olive oil = 84.5 per cent, and sesame oil = 106 per cent. If we divide the iodine absorption of the mixture into two parts, proportional to the iodine absorption of olive oil and sesame oil, we will obtain the proportional quantities of iodine absorbed by each oil contained in the mixture. Thus :

$$\begin{array}{r} 9.64 \\ \hline 84.5 + 106 \end{array} \times 84.5 = 42.8 \text{ absorption due to olive oil.}$$

$$\begin{array}{r} 96.4 \\ \hline 84.5 + 106 \end{array} \times 106 = 53.6 \text{ absorption due to sesame.}$$

In the same way, after obtaining a fair clew to what a mixture contains, one may obtain an approximation for the first result, even though three or four oils are mixed together, but unfortunately the original iodine absorption of the oils in question may be so altered, that the first approximation might yield a mixture quite unlike what one wished to imitate, although the iodine absorption is exactly that of the sample. A mixture of olive, lard, and linseed oils, for example, has an iodine absorption identical with olive oil, viz., 84.5, lard oil being 52.5, and linseed 170. The iodine absorption of such a mixture admits of two interpretations. A mixture of linseed and lard oil may be compounded which shall have the iodine absorption of olive oil, and which, of course, may be mixed in all proportions with olive oil without affecting the iodine absorption, or the calculation may be made as follows :

First Case.

$$\frac{84.5}{52.5 + 170} \times 52.5 = 19.95 = \text{iodine absorption due to lard oil.}$$

$$\frac{84.5}{52.5 + 170} \times 170 = 64.60 = \text{iodine absorption due to linseed oil.}$$

Second Case.

$$\frac{84.5}{84.5 + 52.5 + 170} \times 84.5 = 23.24 = \text{iodine absorption due to olive oil.}$$

$$\frac{84.5}{84.5 + 52.5 + 170} \times 52.5 = 14.44 = \text{iodine absorption due to lard oil.}$$

$$\frac{84.5}{84.5 + 52.5 + 170} \times 170 = 46.75 = \text{iodine absorption due to linseed oil.}$$

In both cases the proportional absorptions for lard oil and linseed oil are the same as demanded by the original iodine absorption. The mixture is then made up as indicated in the second case and examined side by side with the original mixture. Linseed and olive oil both yield insoluble products with sulphur chloride. The lard

oil would be removed by CS_2 , with more or less of the non-solidified products from the other oils, which is subsequently examined by Hubl's reagent.

A. H. W.

Examination of Oils, Fats and Allied Substances.—Thomas T. P. Bruce Warren, Chem. News 62, 179. M. Cailletet proved that the percentage composition of a mixture of two oils could be calculated, when the bromine absorption of the mixture and if its two constituents was known. For example, the solution of turpentine required to decolorize 10 gms. bromine liquor, after digesting with 5 gms. olive oil, is 10.7 gms., and with sesame oil, 4.03 gms., and for a mixture of the two oils, 7 gms.

$$\begin{array}{l} \text{Difference between 7 and 4.03} = 2.97 \\ \text{" " " 7 " 10.70} = 3.70 \end{array} \left. \vphantom{\begin{array}{l} \text{Difference between 7 and 4.03} \\ \text{" " " 7 " 10.70} \end{array}} \right\} \text{Sum of difference} = 6.67.$$

$$\frac{10.7 \times 2.97}{6.67} = 4.76.$$

$$\frac{4.03 \times 3.70}{6.67} = 2.24. \quad \text{Then}$$

$$10.7 : 100 :: 4.76 : 44.53 = \text{olive oil.}$$

14.03 : 100 :: 2.24 : 55.47 = sesame oil, or in a more simplified form:

$$10.7 - 4.03 : 7 - 4.03 :: 100 : x = 44.53.$$

$$10.7 - 4.03 : 10.7 - 7 :: 100 : y = 55.47.$$

Writers on oils have recorded the iodine absorption per cent., which is not well adapted for these calculations, but considering that the unabsorbed iodine has to be estimated to obtain the percentage figures, Cailletet's method of calculating may be rendered available. The Hubl figures form an ascending, and Cailletet's a descending series; consequently when dealing with two oils, we have simply to reverse the figures for the iodine absorption, and the author has taken Cailletet's mixture and adapted it to the known and accepted iodine absorption, in accordance with this arrangement, the Hubl being used in the ordinary way. Call olive oil 106, sesame 84.5, lard 170, and linseed 52.5.

$$106 - 84.5 : 106 - 96.4 :: 100 : 44.65 = \text{olive oil.}$$

$$106 - 84.5 : 96.4 - 84.5 :: 100 : 55.35 = \text{sesame oil.}$$

$$170 - 52.5 : 170 - 84.5 :: 100 : 72.70 = \text{lard oil.}$$

$$170 - 52.5 : 84.5 - 52.5 :: 100 : 27.20 = \text{linseed oil.}$$

$$100 \times 96.4 = (100 - x) 84.5 + 106x \dots\dots\dots (1)$$

$$100 \times 96.4 = (100 - y) 106 + 84.5y \dots\dots\dots (2)$$

whence $x = 55.35$ sesame oil,

$y = 44.65$ olive oil.

$$100 \times 84.5 = (100 - x) 52.5 + 170x \dots\dots\dots (3)$$

$$100 \times 84.5 = (100 - y) 170 + 84.5y \dots\dots\dots (4)$$

whence $x = 27.2$ linseed oil,

$y = 72.8$ lard oil.

Taking the results of (3) and (4) :

$$27.2 \times 170 \text{ (iodine absorption for linseed oil)} = 4634$$

$$72.8 \times 52.5 \text{ (iodine absorption for lard oil)} = \underline{3822}$$

Adding and dividing by 100 = 84.56 = number corresponding to the iodine absorption of the mixture. One must bear in mind in these calculations that the figure given as the iodine absorption is really for 100 parts of that oil, and must not confound the iodine absorption, as the weight of oil required, although it is a measure of the ratio of that oil. In the case of a mixture of two oils, then, if we use the Hubl figure, we must reverse the proportions as regards weights, unless we use the equations 1, 2, 3 and 4.

A. H. W.

NOTES.

The Carbon in Ferromanganese.—Rathke finds (Annalen der Chemie 260, 333) that when ferromanganese is treated with bromine, some carbon tetrabromide, CBr_4 , is formed, and also a carbonaceous substance which contains 49.97 per cent. carbon, 2.12 hydrogen, 21.25 bromine, 1.47 chlorine, and 25.19 oxygen. When this is thoroughly washed and laid upon litmus paper it turns it red. Boiled with sodium carbonate solution, it loses about two-thirds of its bromine and combines with a part of the sodium,

forming a sodium compound. It behaves, therefore, like an organic acid. This carbonaceous substance forms a black granular powder of feeble luster in appearance somewhat like gunpowder. From 30 gms. ferromanganese 3.7 gms. were obtained.

An Acid with a Curious Name.—By oxidizing gallic acid (gallussäure) with copper sulphate in alkaline solution, Boettinger (Annalen der Chemie 260, 337) has obtained a new acid, probably $C_{14}H_{12}O_{11}$ which he calls *Gal acid* (galsäure).

A New Method for Preparing Urea.—Volhard finds (Ann. der Chemie 259, 377) that when potassium cyanide in alkaline solution is treated with a solution of permanganate, added slowly, the mixture being kept at a temperature below 17° , potassium cyanate is formed in large quantity. If ammonium sulphate is now added, and the solution heated, urea and potassium sulphate are formed. The solution is filtered from the manganese hydroxide, the filtrate evaporated to dryness, and the residue exhausted with 95 per cent. alcohol, which dissolves the urea. If any chlorine is present, the urea will contain traces of ammonium chloride, from which it may be purified by dissolving in a little water, evaporating to dryness with a little precipitated barium carbonate and extracting with absolute alcohol. The proportions which Volhard recommends are 39 gms. KCN and 10 gms. KOH dissolved in 100 cc. water, to which a solution of 63 gms. $KMnO_4$ in 1 liter of water is slowly added. This will give 24 gms. urea, or 68 per cent. of the theoretical yield.

The Determination of Egg Constituents Contained in Food.—Bein points out the fact (Ber. 23, 423) that the coloring matters of egg yolk are decomposed by long standing in contact with organic matter; and that dependence cannot therefore be placed upon testing for these coloring substances as a means of detecting egg constituents in a food or other material. Lecithin and glycerin-phosphoric acid are, however, constant constituents. The material to be examined is, therefore, exhausted with ether, the ethereal extract evaporated with addition of a few grains of saltpeter and ignited. The phosphorus is determined in the ash, in which it exists as phosphoric acid. For each 1.12902 gms. phosphoric

acid (= 0.48329 phosphorus) 100 gms. of egg yolk may be assumed to be present.

The Properties of Liquid Chlorine.—The Badische Anilin u. Soda Fabrik have undertaken the manufacture of liquid chlorine. With this object in view, R. Knietzsch has made a careful study of the properties of this substance, the results being reported in full in the *Annalen der Chemie* **259**, 100. Liquid chlorine has a yellow color, inclining to orange. Its sp. gr. at -80° is 1.6602, at 0° 1.4689, at 19° 1.4156, at 40° 1.3490, and at 77° 1.216. Its coefficient of expansion between 15° – 20° is .00203. The pressure of its vapor from 0° to 40° is shown in the following table :

°C.	Pressure in Atmospheres.	°C.	Pressure in Atmospheres.
0	3.660	+ 21.67	6.960
+ 9.62	4.885	+ 29.70	8.652
+ 13.12	5.433	+ 33.16	9.470
+ 20.85	6.791	+ 38.72	10.889

The liquid solidifies at -102° and the critical temperature of the gas is 146° . Knietzsch's paper is a very interesting one, and is well worth reading in full.

NEW BOOKS.

Leffman & Beam's Examination of Water.*—Only two years have elapsed since the first edition of this book was presented to the public. This rapid sale of the first edition was to have been expected in view of the character of the work, and we may safely predict the early appearance of a third edition. The book has been enlarged from 106 to 130 pages. Among the additions made are an account of the methods recommended by the Chemical Section of the American Association for the Advancement of Science, and the application of the Kjeldahl process in the determination of nitrogen. The section upon Purification of Drinking Water has been enlarged, and under the heading Biological Examinations an account of the methods used in examining water for living organisms is given.

**Examination of Water for Sanitary and Technical Purposes*, by Henry Leffman and William Beam. Second Edition. Philadelphia: P. Blakiston, Son & Co., 1012 Walnut Street, 1891.

THE

Journal of Analytical AND Applied Chemistry.

THE DETERMINATION OF CARBON IN STEEL.

BY A. A. BLAIR.

Prof. J. W. Langley has given in his excellent paper,* read at the joint session of the American Institute of Mining Engineers and the British Iron and Steel Institute at Pittsburgh, a clear history of the first part of the work of the American members of the International Steel Standards Committee in their investigation of the various methods for the determination of Carbon in Steel.

As regards the combustion method, the results as stated by Prof. Langley may be briefly summarized as follows: Dr. Dudley showed in a most interesting series of results that the double chloride of copper and ammonium contained some form of organic matter which united with the carbonaceous matter liberated from a steel by the action of this solvent, the amount of the organic matter varying with the purity of the double chloride and diminishing with each crystallization of the salt. The remarkable fact which I discovered that a very acid solution of the double chloride gave higher results than a neutral solution was quickly verified by both Prof. Langley and Dr. Dudley. Dr. Dudley thought that the acid caused a precipitation of organic matter, from the double chloride, while my view was that a neutral solution is rendered slightly alkaline by the solution of the metallic iron and the precipitated copper, and that this alkaline solution dissolves some of the carbonaceous residue which is not subsequently precipitated by the addition of acid.

It was agreed, after the reading of Prof. Langley's paper, that I should continue this investigation, and the results have proved of so much interest to the American Committee that it is deemed

*This Journal, Vol. IV, p. 403.

advisable to make them public now, that the profession at large may have the benefit of the suggestions they offer without undue delay.

My combustion apparatus consists of a platinum tube 26 inches long and 9-16 of an inch in diameter, the forward part inside the furnace being filled for a distance of six inches with granulated oxide of copper held in place by two plugs of platinum gauze. A plug of platinum gauze completely filling the bore of the tube is inserted after the boat and occupies the portion of the tube at the rear of the furnace.

The oxygen and air are contained in cylinders under pressure and each passes through its own purifying apparatus consisting of a bulb containing caustic potassa, 1.27 sp. gr., followed by a 12-inch U tube containing broken pieces of pumice stone. Following each U tube is a tube fitted with a glass stop-cock leading into a T tube which connects directly with the end of the combustion tube. By this arrangement the oxygen and air are under perfect control and there is no danger, as in the ordinary manner of drawing the air through the apparatus by means of an aspirator, of introducing into it any gases that may be in the laboratory. The purifying train for the products of combustion consists of a U tube containing in the limb nearest the combustion tube anhydrous sulphate of copper in pumice, and in the other, turnings of metallic copper, followed by another U tube containing chloride of calcium. In the absorption apparatus, the ends of the Liebig bulb and one end of the tube are fitted when on the balance with short pieces of very fine capillary glass tubing; the other end of the tube is fitted with a cap of rubber tubing, the outer end of which is squeezed together and cemented. This arrangement allows the passage of sufficient air to equalize the pressure in the absorption apparatus, but the capillary openings are too small to permit the loss or gain of moisture during the operation of weighing.

In all cases I used the "factor" weight of the drillings (2.7273 gms.) so that each 0.0001 gm. of carbonic acid obtained in the absorption apparatus is equal to 0.001 per cent. of carbon in the steel.

I determined in the first place to repeat Dr. Dudley's experiments on the recrystallization of the double chloride of copper and

ammonium and therefore prepared a solution by mixing commercial chloride of copper and chloride of ammonium, adding ammonia until a slight precipitate formed, allowing this to settle, syphoning off the clear solution and filtering it through ignited asbestos. This I called solution "A."

Using 200 cc. of solution "A" and 20 cc. hydrochloric acid, I obtained:

No. 1, Carbon	1.046 per cent.
No. 2, "	1.047 "
No. 3, "	1.044 "
No. 4, "	1.049 "

Using 200 cc. solution "A" without the addition of hydrochloric acid, keeping the solution as neutral as possible and washing with acidulated solution "A" to get rid of the basic salts, I obtained:

No. 5, Carbon	1.013 per cent.
No. 6, "	1.004 "

I then evaporated solution "A" and crystallized the double chloride. I washed each crop of crystals with cold water and finally reserved the mother liquor, which I filtered through ignited asbestos, calling it solution "B." The crystals dissolved in water and filtered through asbestos I called solution "C." Using 200 cc. of solution and 20 cc. hydrochloric acid I obtained:

Solution "B."

No. 7, Carbon	1.076 per cent
No. 8, "	1.067 "

Solution "C."

No. 9, Carbon	1.027 per cent.
No. 10, "	1.029 "

I then crystallized about a gallon of the solution which I have in constant use, which is made by dissolving the salt that I buy as "C. P. Crystallized Double Chloride of Copper and Ammonium," in water, adding slight excess of ammonia, allowing to stand for several days, syphoning off and filtering the clear liquid through ignited asbestos. The mother liquor that I obtained I called solution "D," and the solution of the recrystallized salt solution "E," with which I made two determinations, adding 15 cc. hydrochloric acid to one and leaving the other neutral with the following results:

Solution "D."

No. 11, (Acid) Carbon	1.064 per cent.
No. 12, Neutral "	1.022 "

Solution "E."

No. 13, (Acid) Carbon	1.028 per cent.
No. 14, (Neutral) "	0.998 "

I then prepared a solution of chloride of copper by igniting 250 gms. of pure oxide of copper in platinum at a red heat for 30 minutes, dissolving in hydrochloric acid, evaporating to dryness, redissolving in water and filtering through asbestos. The solution which contained 28 gms. of cupric chloride to 100 cc. I called solution "F." With this I made four determinations, two with 20 cc. of hydrochloric acid added to the solution and two with the solution kept as neutral as possible.

Solution "F."

No. 15, (Acid) Carbon	1.034 per cent.
No. 16, " "	1.034 "
No. 17, (Neutral) "	1.034 "
No. 18, " "	1.033 "

It required two days to effect solution in the acid determination and three days in the alkaline, with constant stirring.

I then made four determinations, using 125 cc. of solution "F," 15 cc. hydrochloric acid and 1, 2, 3, and 4 times the molecular equivalent of chloride of ammonium. The latter I made by neutralizing C. P. hydrochloric acid with C. P. ammonia. The results are as follows:

No. 19, (1 equiv. of Chloride of ammonium) Carbon, 1.038 per cent.	
No. 20, (2 " " " "	1.055 "
No. 21, (3 " " " "	1.055 "
No. 22, (4 " " " "	1.073 "

I then fused chloride of potassium and added it to 125 cc. portions of solution "F" with 15 cc. hydrochloric acid, with the following results:

No. 23, (1 equiv. of chloride of potassium) Carbon, 1.036 per cent.	
No. 24, (2 " " " "	1.036 "

Solution of the drillings with the potassium salt is as rapid as

with the ammonium salt, occupying about 20 minutes with the "Special Carbon Standard."

I now determined to try the direct combustion of the steel in oxygen, and for this purpose I had a platinum boat made six inches long and just large enough to go in my combustion tube. I had a cover of platinum foil made for the boat with a half circle cut through about every half inch. On raising these semi-circular pieces to an angle of about 45° they made a series of little wings which directed the current of gas flowing along the top of the tube down into the boat. I selected for this purpose the finer portion of the drillings, and after the combustion I withdrew the boat, ground the magnetic oxide in an agate mortar to expose any metallic particles that might remain unacted upon and burned it a second time. In no case did I get the slightest increase in the weight of my absorption apparatus by the second combustion.

No. 25, Carbon,	1.031 per cent.
No. 26, "	1.020 "
No. 27, "	1.024 "
No. 28, "	1.032 "

Finally I made a determination of carbon by volatilizing the iron in a current of dried hydrochloric acid gas which had been passed through a porcelain tube filled with charcoal and heated to bright redness. This gave me :

No. 29, Carbon	1.024 per cent.
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I then procured from a firm of manufacturing chemists a lot of crystallized double chloride of copper and potassium and made a solution by dissolving 300 gms. of the salt in a litre of water and filtering through ignited asbestos. Using 200 cc. of this solution and 15 cc. strong hydrochloric acid, I obtained :

No. 30, Carbon	1.035 per cent.
No. 31, "	1.038 "

Dr. Dudley's theory of the double chloride of copper and ammonium containing organic matter which is liberated in the treatment of steel, attaching itself to the carbonaceous residue and thus increasing the apparent carbon contents of the steel, seems proved by his own determination as well as by the results Nos. 7, 8, 11, 19, 20, 21, and 22 ; the last four results led me to believe, however,

that this organic matter comes from the chloride of ammonium and is a hydrocarbon derived from the gas liquor from which all ammonia salts are now made.

My own theory that the copper solution must be strongly acidified to give correct results, received strong support from the determinations Nos. 5, 6, 12, and 14; for these as well as my previous determinations point strongly to a solution of the carbonaceous matter by the alkaline salts in the absence of an excess of acid. The striking results obtained from the chloride of copper solution "F" show plainly that an excess of acid does not cause a loss of carbon while it very much facilitates the solution of the steel. I then obtained from Prof. Langley some very fine drillings of the same steel and using the six inch boat described above I obtained:

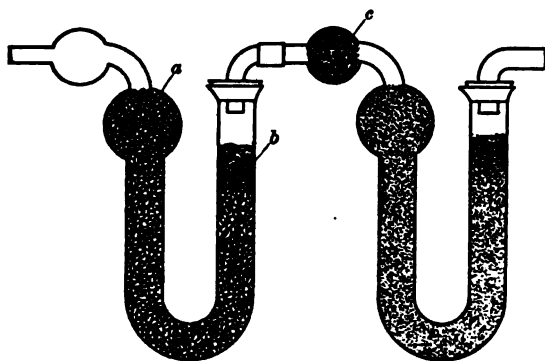
No. 32, Carbon	1.032 per cent.
No. 33, "	1.030 "
No. 34, "	1.031 "

To test the effect of using a purifying apparatus that had been used for combustions of the carbonaceous residue liberated by the double chloride, I made several combustions of these residues and, without changing the apparatus, a direct combustion. The result was :

No. 35, Carbon	1.042 per cent.
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This last result taken in connection with many others that I had previously obtained suggested to me the desirability of using some substance in my purifying apparatus that would not only prove more efficient but would render unnecessary the constant changes and delays involved by a number of sets of purifying tubes and the necessity for changing the anhydrous cupric sulphate in pumice. It has been my practice to use one set of purifying tubes for three combustions only, then to substitute another set and while this was in use to purify the first set by placing the limb of the U tube that contained the cupric sulphate in a copper box, heat the box to about 200° C. and draw air, previously dried by passing it through a jar of chloride of calcium, through the apparatus. I, therefore, instituted a series of experiments on this subject, being finally led to try cuprous chloride, on the theory that small amounts of hydrochloric acid gas and chlorine when brought

in contact with cuprous chloride would be absorbed, the chlorine oxidizing the cuprous to cupric chloride, I then prepared a purifying train consisting of two Marchand U tubes, the first of which contains in the bulb "a" granulated dried cuprous chloride, made



by moistening the ordinary powdered salt and stirring it while drying in a capsule, until it forms into little lumps about the size of a split pea. After heating it until all the moisture is expelled it is transferred,

while still hot, to the U tube, completely filling the bulb "a." The rest of the U tube is filled with anhydrous cupric sulphate made by heating small crystals of the ordinary salt until the water is expelled and the salt is white. At "b" is placed a plug of asbestos to prevent small particles of cupric sulphate from being carried forward with the current of gas. The second U tube is filled with *dried* not fused, chloride of calcium, as the latter is apt to contain caustic lime. Cupric sulphate absorbs its own volume of hydrochloric acid gas, giving it up only when heated. With the tubes thus filled I made four combustions on the "Special Carbon Standard Ingot," using the double chloride of copper and potassium and washing No. 36, 37, and 38 with hot hydrochloric acid and water, and No. 39 in the usual way, using cold water and acidulated double chloride. Mr. Shimer thought that by washing with hydrochloric acid and hot water there was less hydrochloric acid left in the carbonaceous residue, and I wanted to see whether there was any possibility of getting lower results in this way, due to the action of the acid and hot water on the carbonaceous residue.

No. 36, Carbon	1.030 per cent.
No. 37, "	1.029 "
No. 38, "	1.033 "
No. 39, "	1.026 "

The results were all low, and I should have been inclined to refer it to the method of washing but that No. 39, washed in the usual way, was the lowest of all. It then occurred to me that anhydrous cupric sulphate being much more hygroscopic than chloride of calcium, the oxygen and air left the absorption apparatus with more moisture than they had when they entered it, after passing through the purifying train. If this were true then the greater the volume of oxygen and air passed through the apparatus, the lower the result. To prove this I made a direct combustion on the fine sample, the time occupied being about 90 minutes instead of the usual 35 minutes necessary to burn the carbonaceous residue. The combustion followed immediately after No. 39, the result being:

No. 40, Carbon 1.006 per cent.

This seemed quite conclusive as to the cause of the low results, and to overcome the difficulty I introduced a small plug of cotton into the bulb "c" of the chloride of calcium tube and moistened it with one or at most two drops of water. Another direct combustion on the fine sample gave:

No. 41, Carbon 1.037 per cent.

I then made a number of combustions in the course of my ordinary work, removing the plug of cotton in "c" after each day's work and putting in a fresh one duly moistened before each new set of combustions. After the lapse of several days I made two more determinations on the "Special Carbon Standard Ingot," No. 42 on the carbonaceous residue and No. 43 a direct combustion. They were respectively the fourth and fifth combustions of a series made at one time, and No. 43 was the twenty-third combustion made without heating the purifying apparatus.

No. 42, Carbon 1.038 per cent.

No. 43, " 1.037 "

I am led to conclude that chloride of copper and potassium is a much more safe and desirable solvent to use than chloride of copper and ammonium, and unless subsequent experience shall show some flaw in my work, cuprous chloride and anhydrous cupric sulphate are much more convenient and much safer reagents for purifying the gas than any substances previously used.

This series of experiments illustrates in a striking way the value of a "Standard" in work of this character. The carbon once established in a sample, each experiment has an increased value, for the result is known to be not only a departure from the mean of many analyses, but a variation from the absolute amount. The value of a method or the efficiency of an arrangement of apparatus is thus made evident at once and the error is much more readily referred to its real source than would otherwise be possible.

Analytical chemists all over the world will owe Prof. Langley a debt of gratitude not only for his suggestion that led to the establishment of the International Committee but for his subsequent work which has made it possible to carry out his original idea.

PHILADELPHIA, FEB. 16, 1891.

LABORATORY OF BOOTH, GARRETT & BLAIR.

NOTES ON CARBON IN "EXPERIMENTAL STANDARD."

BY P. W. SHIMER.

My first results on the "Experimental Standard" distributed by Prof. J. W. Langley among the members of the American Committee on International Standards of Iron and Steel, were 1.055 per cent. carbon in the sample marked "Ingot," and 1.052 carbon in the sample marked "Hammered." These results were obtained by use of double chloride of copper and ammonium solutions and combustion in a porcelain tube with the usual purifying apparatus, including anhydrous copper sulphate tube. These determinations were made before it was known that the double chloride usually contains carbonaceous matter. The copper solution was made as nearly neutral as possible before using.

After Dr. Dudley had shown that the results obtained by use of the double chloride of copper and ammonium could be varied by varying the method of making the double chloride, I endeavored to determine the absolute total carbon by direct combustion of the steel in a current of oxygen. Owing to the length of time required to make a direct combustion in a porcelain tube (4 to 6 hours), these efforts were not successful. The combustions were made on the "Ingot," reduced by grinding until part of the sample passed through a 35-mesh sieve. This fine material was then burned in oxygen in a porcelain tube. In some of the experiments the steel was intimately mixed with coarsely crushed Fe_2O_3 , previ-

ously ignited to constant weight in oxygen. In other experiments CuO was used in place of Fe_2O_3 . In still other cases, a long copper boat, previously ignited to constant weight in oxygen, was used. The powdered steel was evenly and thinly spread on the bottom of the boat, which the ignition had covered with a coating of CuO. The results of six combustions were: 1.072, 1.058, 1.077, 1.065, 1.076, 1.072. These results were not worthy of confidence, because of the strain upon the constant weight of the potash bulbs by reason of the long combustion of 4 to 6 hours. Suspecting that the oxygen might contain a trace of carburetted gas not absorbed by KOH solution, I placed a second porcelain tube containing CuO directly above the combustion tube in the furnace. On making a combustion, the oxygen was first passed through the upper tube, then through KOH, then into CaCl_2 tube and combustion tube. In this way a good constant weight could be maintained for long combustions. By this arrangement a direct combustion, requiring five hours, gave 1.047 per cent. carbon in the "Ingot."

If the double chloride of copper and ammonium contains carbonaceous matter, it occurred to me that it might perhaps be removed by filtration of the solution through charcoal. For this purpose a glass tube 27 inches long was filled with crushed charcoal, and the copper solution was slowly filtered through it, being finally passed through ignited asbestos to remove minutely divided carbon in suspension. Samples of 3 gms. each of the "Ingot" were dissolved in 200 cc. of the above filtered copper solution previously made acid by addition of 10 cc. HCl, sp. gr. 1.12. The results were: 1.036, 1.034.

The original copper-solution, without filtration through charcoal, was then used in the same way. The result was 1.040. This difference is not large enough to have any decisive significance. But it will be worth while to try the effect of filtration through charcoal upon a more impure sample of the double chloride than mine happened to be.

I next tried the double chloride of copper and potassium as a solvent in the manner recommended by Mr. Blair. The results were: 1.036, 1.038.

After the solution of the steel in the above five determinations, the carbon residues were filtered upon ignited asbestos (without use of suction) in Dr. Drown's wide-necked carbon funnels. (This Journal 2, 330.)

When the carbon was all in the funnel, the asbestos was liberally soaked with cold HCl, sp.gr. 1.12, and allowed to remain in this condition for a few minutes, in order that all chlorides might be rendered easily soluble. The carbon was then washed (without suction) with hot water, 20 to 30 times, until the filtrate showed no chlorine by silver nitrate. After drying at 90° C., the carbons were transferred to the porcelain combustion tube, which contained nothing but the usual CuO. The apparatus was put together in the following order: 1. Oxygen tank; 2. Porcelain tube containing CuO, placed immediately above the combustion tube in the furnace; 3. KOH bulbs; 4. CaCl₂ tube; 5. Combustion tube containing CuO; 6. A Liebig potash bulb containing nothing but a drop of water in each of its five bulbs, and cooled by filter paper kept wet by dipping in cold water; 7. CaCl₂ tube; 8. KOH bulbs with the usual CaCl₂ tube attached; 9. A guard of CaCl₂. After completing the above five combustions, the few drops of water were removed from the Liebig bulbs and found to contain no chlorine when tested by silver nitrate. Evidently the method of washing the carbon residue (by liberal treatment with HCl and thorough washing without suction) has removed all chlorides, for any hydrochloric acid or chlorine escaping from the combustion tube would be condensed or absorbed in the cold and moist Liebig bulbs. I cannot help thinking that a too sparing use of HCl on the carbon residue, and a too rapid washing by suction, is responsible for much of the trouble with hydrochloric acid and chlorine. In order that wash-water may thoroughly dissolve impurities, it must be given time to act upon them. From the fact that the results obtained as detailed agree so closely with the results obtained in the admirable apparatus devised by Mr. Blair, I am still further encouraged to believe that the HCl difficulty may perhaps be overcome at its source by washing in the manner described, and, as a further precaution, by the use of some simple condensing and absorbing arrangement, like the moistened Liebig bulbs. More experiments must, however, be made to decide these points.

A NEW RETORT STAND.

BY EDWARD HART.

Compactness in the apparatus used in a laboratory is of great advantage, and sometimes it is essential. With one of my classes I have been compelled to study this matter very carefully, because the amount of room available was too small. In this way I have been led to devise a piece of apparatus which answers all the purposes of a retort stand, is inexpensive and can be stored in a drawer. The result is shown in the cuts figured below. In this laboratory the desk shelves are supported by upright strips of inch pine board, and the base of the ring clasps this upright and is fastened by means of a flat-headed screw. To prevent this from defacing the upright piece and also to give a better grip, a bent piece of strap iron is inserted in a groove provided for it and the screw forces this against the upright piece.* The only disadvantage in the use of this apparatus is its immobility the retort ring

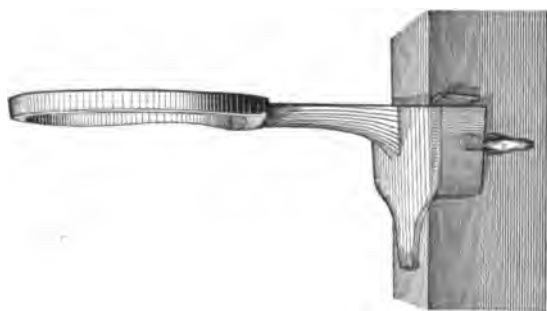


FIG. 1.

can be moved up and down, but the stand must remain in one fixed position. It would be easy, however, to construct a movable wooden stand.

Fig. 1 shows the ring in position, and Fig. 2 gives a better idea of the way it is fastened to the upright piece.



FIG. 2.

* This casting was made for me by Jacob Wilson of Easton, Pa., who will supply it for 25 cents. \$2.50 a dozen.

THE ELECTROLYTIC ASSAY OF COPPER.

BY STUART CROSSDALE.

Electrolysis, like other methods of analysis, began with qualitative tests. As early as 1807 Sir Humphrey Davy,* in a lecture before the Royal Society on "Some Chemical Agencies of Electricity," makes the following statement. "In an experiment that I made, electrifying a mixed solution of muriates of iron, of copper, of tin and of cobalt in a positive vessel, distilled water being in a negative vessel, all the four oxides passed along the asbestos, and into the negative tube, and a yellow metallic crust formed on the wire, and the oxides arranged themselves in a mixed state round the base of it." This was probably the first record of metals being deposited from solution by the electric current. In 1830 Edmund Davy† applied this method in the detection of arsenic, mercury, lead, and copper in foods, and other vegetable and animal substances. The current was produced by a voltaic couple of platinum and zinc placed in the acid solution of the substance to be tested.

Similar experiments were performed by Prof. Daniel,‡ Gaultier de Claubry,§ Bloxam,|| and Nickles.¶ Depretz in 1857 electrolyzed the acetates of copper and lead and found that the copper deposited on the negative pole while the lead separated as the peroxide on the positive pole. The same thing he observed to be true when a solution of the nitrates was used.

A method for the quantitative determination of copper by electrolysis was first published by Dr. Gibbs** in 1864. A solution of the sulphate was electrolyzed in a weighed platinum dish which formed the negative electrode. The end of the precipitation, which occupied from one to three hours, was determined by testing a drop of the solution on a porcelain plate with a drop of sulphuretted hydrogen water. The precipitated copper was washed with distilled water, dried in a vacuum over sulphuric acid, and weighed

* *Philos. Trans.* 1807, 55; *Proceed. Royal Soc.* 1807, 247.

† *Philos. Trans.* 1831, 147; *Proceed. Royal Soc.* 1830, 5.

‡ *Philos. Trans.* 1839, 97; 1840, 209.

§ *Jahresbericht* 1850, 602.

|| *Kopp & Wills Jahresbericht* 1860, 645; 1862, 597; *Pharm. Jour.* 2nd series 3, 528; 3, 607; *Chem. Soc. quar. J.* 13, 338; *Ztschr. für anal. Chem.* 1, 483; *Ding. Poly. Jour.* 177, 231.

¶ *Kopp & Wills Jahresbericht* 1862, 610; *Ding. Poly. Jour.* 177, 231.

** *Ztschr. anal. Chem.* 3, 334; *Am. Jour. Sci. and Arts*, 2nd series 39, 64.

with the dish. The method gave accurate results with a solution of the pure sulphate, and with a similar solution of copper and nickel.

The following year Luckow* published a paper entitled "Elektro-Metall-Analyse," in which he gives a detailed description of the detection and determination of a large number of metals by electrolysis. He claims to have used this method for twenty years previous to its publication, and to have determined copper quantitatively by it as early as 1860. The method employed was essentially the same as the one just described. Two new points, however, were mentioned for the first time: 1st, the excess of free acid in the solution to be electrolysed was neutralized with potash, soda, or magnesia instead of evaporated to dryness; and 2nd, the copper, after being washed with water, was washed once with alcohol and dried at 100°. Ullgren† (1866) states that the method "is not rapid, and the copper is not completely precipitated. During the winter of 1866-'67, S. P. Sharpless‡ confirmed the work of Gibbs, and recommended neutralizing the excess of free acid with ammonia instead of evaporating to dryness. Some one suggested burning off the alcohol adhering to the dish after washing, instead of drying at 100°. This was done with satisfactory results.

Lecoq de Boisbaudran§ found the electrolytic method to be inaccurate when the solution of copper is very dilute; also in the presence of ferrous, or large quantities of other salts. Free hydrochloric and chlorous acids were found to attack the platinum when decomposed by the current. Two years later|| he repeated his work, and recommended washing the copper (from a ferrous sulphate solution) with dilute sulphuric acid, and finally with hot water while the current was running. He also found that, other things being equal, the amount of copper held in solution is proportional to the amount of ferrous sulphate present, and from this he constructed a table of corrections.

The same year Luckow¶ received honorable mention from the

*Ding. Poly. Jour. 177, 231; 191, 149.

†Jour. f. prakt. Chem. 102, 477; Ztschr. f. anal. Chem. 7, 255.

‡Trans. A. I. M. E. 10, 65; 11, 133.

§Bull. Soc. Chim. 1867, 468; Ztschr. f. anal. Chem. 7, 253.

||Bull. Soc. Chim. 1869, 35; Ztschr. f. anal. Chem. 9, 102.

¶Ztschr. f. anal. Chem. 8, 23.

Mansfield Copper Works for a new electrolytic method, in which he substituted a nitric acid solution (0.1 gm. HNO_3 to 1 cc.) containing a few drops of tartaric acid, for a solution of the sulphate. He claimed accuracy for the method in the absence of tin, antimony, arsenic, mercury and bismuth. Silver was reduced to the metallic state by the tartaric acid, and could be removed. Lead and manganese were deposited as peroxides on the positive pole, and the other metals were not precipitated.

The work of Gibbs was again confirmed in 1871 by Merrick.* In a later communication† he recommended, for accurate work, treating the solution of the ore with sufficient ammonia to precipitate and redissolve the copper; then filtering off the silica, iron, alumina, etc., and precipitating the copper from the solution by electrolysis, after strongly acidifying with sulphuric acid. The directors of the laboratory at Eisleben have published papers‡ from time to time on Luckow's nitric acid method. The addition of oxalic acid is recommended instead of tartaric acid, especially with substances containing large amounts of iron.

Oeschger and Mesdach,§ Herpin,|| Wrightson,¶ and Kowalsky** separated copper from the other metals by the methods just described.

In 1878 Schutzenberger†† submitted a solution of acetate of copper, that had been rendered slightly basic by boiling, to electrolysis, and obtained allotropic copper, together with a little acetate and oxide. This deposit was brittle, had a bronze color, and oxidized readily.

Weidemann observed this as early as 1856,‡‡ and states§§ that the peculiar properties are due to the presence of an oxide.

*Am. Chemist 2, 136; Chem. News 24, 72, 100.

†Chem. News 25, 155.

‡Ztschr. f. anal. Chem. 11, 1; 13, 179; 14, 350; Am. Chemist 3, 370; Jour. Chem. Soc. 1872, 925; Berg-u. Hütten Zeit. 34, 155; Chem. Centralb. 3 ser. 6, 557.

§Bull. Soc. Chim. 23, 180; Ztschr. anal. Chem. 14, 192.

||Ding. Poly. Jour. 215, 440; Bull. Soc. Encourag. 1874, 595; Zeitschr. anal. Chem. 15, 335; Moniteur Scientif. 3rd ser. 5, 41.

¶Ztschr. anal. Chem. 15, 297; Ding. Poly. Jour. 225, 67; Jour. Chem. Soc. 1877, Part 1, 340.

**Bull. Soc. Chim. 27, 555.

††Comp. Rend. 86, 1265, 1397; Jour. Chem. Soc. 34 [1878], 706, 840; Chem. News, 37, 274; Ding. Poly. Jour. 230, 307; Beib. Annal. d. Chem. u. Phys. 3, 514; Bull. Soc. Chim. 31, 291; Ber. 12, 277, 1016.

‡‡Pogg. Annal. 99, 193.

§§Annal. d. Chem. u. Phys. 6, 81; Ding. Poly. Jour. 230, 307; Chem. Centralb., 3d series, 10, 145.

Riche* and Ohl† used the methods first described. In any of these methods the amount of acid anhydride should not exceed 8 per cent. by weight of the solution used for the assay. Copper may be deposited completely from a hydrochloric acid solution by the addition of ammonium chloride, ammonium acetate, or sodium chloride; and from a neutral solution by the addition of ammonia, ammonium carbonate, or potassium cyanide. (Luckow.‡)

Mackintosh,§ in experimenting with Luckow's nitric acid method, found that the copper deposited contained carbon, hydrogen and nitrogen, which were determined quantitatively; and concluded, "that some organic matters, and in all probability all, in the presence of nitric acid in the copper solution undergoing electrolysis, cause erroneous results; and that from a nitric acid solution with no organic matter, it is extremely difficult to separate all the copper." He also found Schutzenberger's allotropic copper to contain carbon and hydrogen. Luckow,|| in reply, states that tartaric acid was added to prevent the injurious action of manganese during the precipitation of the copper, but in ordinary cases should not be used; and that the copper is completely deposited from a nitric acid solution if no nitrous fumes are present and a weak current is used.

Moore¶ determined copper quantitatively by electrolysis from a solution in potassium cyanide.

Classen and Reiss** used a solution of the double oxalate of copper and ammonium, to which had been added an excess of ammonium oxalate.

The following chemists experimented with, or used in actual practice, the electrolysis of the nitrate or sulphate: Gore,†† C. F.

*Annal. de. chim. et Phys., 3d series, 13, 508; Am. Jour. Sci. and Arts, 3rd series, 16, 320; Ding. Poly. Jour. 243, 248; Ztschr. anal. Chem. 21, 116.

†Ztschr. anal. Chem. 18, 533; Chem. News 41, 25; Jour. Chem. Soc. 38 [1880], 583; Chem. Centralb., 3rd series 10, 812.

‡Ztschr. anal. Chem. 19, 14; Ding. Poly. Jour. 239, 307; Chem. News 41, 213; Beib. Annal. d. Chem. u. Phys. 4, 140; Chem. Central. 3rd series 11, 55; Ber. 13, 440.

§Trans. A. I. M. E. 10, 57; Am. Chem. Jour. 3, 354; Chem. News 44, 279; 45, 101; Jour. Chem. Soc. 42 [1882], 428, 660; Beib. Annal. d. Chem. u. Phys. 6, 393; Ding. Poly. Jour. 244, 171; Chem. Centralb. 13, 59; Ztschr. anal. Chem. 23, 67; Chem. Ztg. 6, 282; Ber. 15, 87; Jour. Soc. Chem. Ind. 1, 118.

||Chem. Ztg. 6, 23, 43; Chem. News 45, 101.

¶Chem. News 53, 209; Jour. Chem. Soc. 50 [1886], 921; Chem. Centralb. 17, 647.

**Ber. 14, 1622; Chem. News 46, 105; Jour. Chem. Soc. 39 [1881], 1087; Bull. Soc. Chim. 37, 184; Chem. Centralb. 12, 668; Ztschr. anal. Chem. 21, 255.

††Nature 25, 473; Beib. Annal. Chem. u. Phys. 6, 394.

Chandler,* W. H. Chandler,† Eggleston,‡ Glenn,§ Booth, Garrett & Blair,|| Hunt,¶ Nichols & Co.,** Richards,†† (after separating the copper as a sulphide), Stillwell & Gladding,‡‡ Eustis,§§ Stillman,|||| Akerblom¶¶ (after separating the copper as sulphide), Pufahl,*** Killian,††† Stahl,‡‡‡ Habirshaw,§§§ Westmormland,||||| Haddock,¶¶¶¶ Shand,**** and Torrey & Eaton.†††† Some of the results obtained were unsatisfactory, and will be mentioned under the separation of copper from other metals. Classen‡‡‡ used a solution of the double oxalate of copper and ammonia, except in separating some metals of the silver and copper groups.

Soret§§§§ found that electrolytic copper, obtained from an acid solution, occluded hydrogen and carbon dioxide in small quantities.

Smith and Frankel¶¶¶¶ made a number of separations from a solution of the double cyanide of copper and potassium. Classen and Scheele***** recommend the addition of oxalic acid to dilute solutions of the double oxalate for electrolysis; concentrated solutions

*Trans. A. I. M. E. 11, 126.

†Ibid 11, 126.

‡Ibid 11, 128.

§Ibid 11, 129; Feb. 1889; this Jour. 3, 342.

||Ibid 11, 126.

¶Ibid 11, 131.

**Ibid 11, 131.

††Ibid 11, 133.

‡‡Ibid 11, 134.

§§Ibid 11, 124.

||||Ibid 11, 125.

¶¶Ding. Poly. Jour. 255, 533.

***Ding. Poly. Jour. 252, 211.

†††Ztschr. anal. Chem. 25, 403; Chem. News 54, 84.

‡‡‡Ding. Poly. Jour. 262, 277; Jour. Chem. Soc. 52 [1887], 529.

§§Trans. A. I. M. E. 11, 130.

||||Jour. Soc. Chem. Ind. 5, 55.

¶¶¶Ibid 5, 54; Pharm. Jour. [3], 10.

****Pharm. J. Trans. [3] 17, 750; Jour. Chem. Soc. 52 [1887], 1000.

††††Peter's "Modern Methods of Copper Smelting," p. 25.

|||||Ber. 14, 1627, 2782; 17, 2469; 18, 1787; 21, 366, 368; Am. Jour. Sci. and Arts, 3rd series, 29, 164. Ding. Poly. Jour. 259, 92; Bull. Soc. Chim. 44, 268; 50, 64; Jour. Chem. Soc. 48 [1885], 1095; 54 [1888] 528; Ztschr. anal. Chem. 25, 113; Chem. News 48, 149; Jour. Soc. Chem. Ind. 7, 344, 402; this Journal 3, 70, 71.

Comp. Rend. 107, 733, 946; 108, 1298; Chem. News 60, 24; Jour. Chem. Soc. 56 [1889], 105; Chem. Centralb., 4th series 1, 278.

|||||Am. Chem. Jour. 11, 264; 12, 104, 428; Ber. 22, 602 R; Ztschr. anal. Chem. 29, 680; Chem. News 60, 102, 262; Jour. Chem. Soc. 56 [1889], 797; 58 [1890], 665, 1029; Chem. Centralb., 4th series 2, 267; Bull. Soc. Chim., 3d series 4, 604; Jour. Soc. Chem. Ind. 9, 656; this Journal 3, 254, 416.

****Ber. 21, 2892; Jour. Chem. Soc. 56 [1889], 77; Bull. Soc. Chim. 51, 151; Chem. Centralb. 1888, p. 1588; Jour. Soc. Chem. Ind. 8, 137.

should be nearly neutral to prevent the separation of copper oxalate.

Brand* experimented on the electrolysis of an alkaline solution of the double pyrophosphates, but with copper the method proved unsatisfactory.

Smith† obtained much better results from an acid solution of the orthophosphates.

Rüdorff‡ recommends using an ammoniacal solution of copper to which 2 or 3 gms. of potassium or ammonium nitrate have been added.

The foregoing summary includes all the important methods that have been published for the electrolytic assay of copper. On looking over the original papers, it will be noticed that most of them are taken up with the precipitation of copper and the separation of the same from other metals. A number of general methods are given, which can be applied to ordinary cases, but the literature concerning special separation is scattered, and no method in detail for the separation of copper from all the metals that are liable to be precipitated under the same conditions has been given. More than this, some English chemists§ have recently doubted the accuracy of the battery assay as applied to copper.

Under these circumstances I have been led to perform the following experiments, with the hope of arranging a method that can be applied to alloys and ores that are met with in common practice.

The first experiments were on a solution of pure copper, to ascertain the most favorable conditions and necessary precautions with which to work, these were followed by the separation of copper from the metals with which it is usually associated.

Pure copper was prepared by the electrolysis of the sulphate, using platinum foil greased on one side for the negative electrode. When the copper deposited was of sufficient thickness, the foil was stripped off and the copper broken in small pieces. These were

*Chem. News 61, 17; Jour. Chem. Soc. 58 [1890], 294; Ztschr. anal. Chem. 28, 591; Ber. 22, 774 R.; Jour. Soc. Chem. Ind. 8, 1011.

†Am. Chem. Jour. 12, 329; Chem. Centralb., 4th series 2, 76; Bull. Soc. Chim., 3rd series 4, 603; Jour. Chem. Soc. 58 [1890], 1028; Ber. 23, 600 R.; Jour. Soc. Chem. Ind. 9, 898.

‡Ber. 21, 3050; Bull. Soc. Chim. 52, 60; Jour. Chim. Soc. 56 [1889], 188; Chem. Centralb. 1888, p. 1592; Jour. Soc. Chem. Ind. 8, 62; this Journal 3, 72.

§Chem. News 58, 76, 108, 131.

treated with dilute nitric acid until a violent reaction took place, and then they were washed with distilled water, and finally with alcohol; the adhering alcohol was burned off and the copper kept in a desiccator until used.

The assays were made from a solution of the sulphate containing free sulphuric acid.

Both cylinders and dishes were used for the negative electrodes. The former are convenient to wash with the current running, and do not catch any dust that may drop into the solution, or oxides that may form in excess on the positive pole. Their disadvantage lies in the fact that the copper is often deposited in a spongy condition around the edge of the cylinder and is easily rubbed off in subsequent handling. They can be used only for very small amounts of copper. Dishes were found to be the more satisfactory, and were used for the greater part of the work.

The sulphuretted hydrogen test is commonly used to determine the end of the precipitation. Although this is said to be extremely delicate,* the following experiments show it to be inaccurate when only a drop of the solution can be tested, especially if much free acid is present.

No.	Copper Used. Gms.	Copper found when H ₂ S gave no reaction. Gms.	Copper found in filtrate. Gms.	Total Copper deposited. Gms.
(1)	0.0541	0.0521	0.0019	0.0540
(2)	0.0540	0.0527	0.0013	0.0540
(3)	0.0490	0.0474	0.0016	0.049
(4)	0.0483	0.0431	0.0052	0.0483
(5)	0.0730	0.0716
(6)	0.0603	0.0595	0.0008	0.0603
(7)	0.0550	0.0538	0.0012	0.0550
(8)	0.1038	0.1033	0.0005	} Loss in weight. Copper in filtrate not determined.
(9)	0.1038	0.1033	0.0005	
(10)	0.1033	0.1024	0.0009	
(11)	0.1033	0.1029	0.0004	

Diluting the solution and thus exposing a new surface of the electrode is a more accurate and a more convenient test.

When the electrolysis takes place in an acid solution it is necessary in most cases to wash the precipitated copper while the current is running. When a solution of the sulphate, free from

*School of Mines Quarterly, July, 1887. This Journal 1, 358.

nitric and hydrochloric acids is used, it is possible to wash one, and, if the facilities for shifting and regulating the current are good, it is possible to wash a number of assays after the circuit is broken and yet obtain good results, as for example ;

No.	Copper Used. Gms.	Copper Found. Gms.
(12)	0.0533	0.0533
(13)	0.0471	0.0471
(14)	0.0667	0.0667
(15)	0.0456	0.0456

To obtain these results the washing must be done rapidly. It is however, advisable to wash with the circuit closed under all circumstances. *Cold* water must always be used for washing from an acid solution whether the circuit be closed or open. The following experiment will illustrate this point.

No.	Copper Used. Gms.	Copper Found. Gms.	Loss in Weight. Gms.
(16)1377	.1372	.0005

The copper was washed with hot water while the current was running. The *filtrate* contained no copper but the *washings* gave a decided test for that metal.

After washing with water, the assays were washed once with alcohol and that which adhered to the dish was burned off. The dishes were then placed in desiccators and allowed to cool, after which they were placed in the balance case for five or ten minutes and weighed.

The balance used for this work was one made by Becker Bros. It was sensitive to 0.1 mg. when loaded to 100 gms. The source of the electric current was a battery of gravity cells.

(To be Continued.)

THE PRECIPITATION OF MANGANESE AS AMMONIUM MANGANOUS PHOSPHATE.*

BY ALEXANDER G. MCKENNA.

In the determination of manganese in iron ores, it is customary to precipitate the manganese as dioxide, after separation from the sesquioxides by the basic acetate process, by adding bromine to

*Technology Quarterly, 2, 333.

the filtrate from the acetic acid precipitation. The manganese thus thrown down may be ignited and weighed as manganese proto-sesquioxide, but the results are inaccurate from two causes. Manganese dioxide when precipitated in the presence of sodium or potassium salts always carries down with it some alkali, which appears to be chemically combined with the manganese, since it cannot be removed by the most prolonged washing with water.*

This source of error can be avoided by using ammonium acetate in the basic separation, but in this case the solution must be made alkaline before manganese can be precipitated by bromine, and the separation from calcium is then rendered less sharp.

Another objection to the determination of manganese based on the ignition of the precipitated dioxide is the uncertainty of the resulting oxide, which is generally assumed to be Mn_2O_3 . Pickering† has shown that the percentage of manganese in this oxide varied between 69.69 per cent. and 75 per cent., according to the temperature of ignition and other causes.

It is now customary to redissolve the manganese dioxide in hydrochloric acid, and then precipitate it as ammonium manganous phosphate. The precipitate is ignited and weighed as manganese pyrophosphate. This method of determining manganese, which we owe to Dr. Wolcott Gibbs, is now generally admitted to be the most accurate as well as the most easily performed of all the methods of determining manganese. It has been previously modified by many chemists, but none of these modifications seem to possess any advantages over the original process as given by Dr. Gibbs.

The following work was undertaken at the suggestion of Dr. T. M. Drown, to determine if some of the proposed changes in the details of the process were of any advantage in simplifying the method or enhancing its accuracy.

Two solutions of manganous chloride were prepared, and measured portions were taken for precipitation. In the first method, Gibbs' original directions were followed.‡ The precipitation was made in a platinum dish, by adding a solution of sodium hydro-

*See Wright and Menke on Manganese Dioxide, in the Journal of the Chemical Society for 1880, p. 23.

†Chem. News, Vol. XLIII. p. 226.

‡Am. Journal of Science [II.], Vol. XLIV. p. 216.

gen phosphate in excess. The white precipitate which formed was dissolved in hydrochloric acid, the solution heated to boiling, and ammonia added in excess. The solution was now boiled for ten minutes and allowed to stand near the boiling point for one hour. It was filtered hot, and washed with hot water.

In the second method, Blair's* directions were followed. The solution was made acid with hydrochloric acid, an excess of sodium hydrogen phosphate added, the solution brought to boiling in a platinum dish, and ammonia added drop by drop, with constant stirring, until further addition of a drop of ammonia made no change in the silky character of the precipitate; a dozen drops more of ammonia were added, and after boiling a minute longer the solution was cooled in ice water before filtering. The wash water used was made by dissolving ten grams of ammonium nitrate in 100 cc. of slightly ammoniacal water.

The chief object in view in the third method was to discover if there is any valid objection to making the precipitation in glass, and also to determine the length of time required for complete precipitation. To the solution of manganese salt in a beaker, hydrochloric acid and sodium hydrogen phosphate were added. The solution was heated to boiling, and 20 cc. ammonia water added. The boiling was continued three minutes, with constant stirring, which is absolutely necessary to prevent bumping. The wash water used was made by adding one volume of ammonia (sp. gr. 0.96) to three volumes of water. Following are the results obtained in this series of analyses.

Comparison of Results Obtained by the Three Methods.

	Gibbs's Original Method.	Blair's Method.	Precipitation in Glass and washing with Ammonia Water.
	Grams.	Grams.	Grams.
Weight of Manganese Pyrophosphate obtained, first solution	{ .4990 .4996	.4997 .4992	.4994 .5007
Do., second solution0897	.0896	.0894

Three more determinations were made by precipitation in glass.

*The Chemical Analysis of Iron, p. 93.

but the precipitates did not become crystalline in three minutes, and the washings were turbid.

The manganese precipitates after ignition were examined for silica, but none was found.

This set of experiments seems to show that essentially the same results are obtained by following either Gibbs' or Blair's directions; also that glass is not attacked by the solution in three minutes boiling, but that this time is not always sufficient to insure the complete conversion of the precipitate to the crystalline form which is necessary before filtration.

Another series of experiments was made in the same manner, but with a different amount of manganese.

Second Series of Results.

	Gibbs's Method.	Blair's Method.	In Glass as before.
	Grams.	Grams.	Grams.
Weight of Manganese Pyrophosphate obtained	.2415 .2427 .2408 .2432 .2355*	.2432 .2432 .2385 . . . * . . . *	.2412 .2427 .2425 .2387*

These results confirm those in the first series, and indicate the necessity of having the precipitate thoroughly crystalline.

The amount of manganese in the filtrates and washings of each set of these experiments was determined, (except in those cases where the precipitate was not crystalline,) with the following results. The total volume of the filtrate and washings was in each case about 300 cc.

Solubility of the Precipitate.

	Gibbs's Method. Washed with Water.	Blair's Method. Washed with Dilute Ammonium Nitrate.	In Glass. Washed with Dilute Ammonia.
	Average Gram.	Average Gram.	Average Gram.
Filtrate contained Metallic Manganese0005	.0004	. . .
Washings contained Metallic Manganese.0005	.0012	.0003

*Not crystalline.

In order to determine the relative value of the three wash waters under precisely the same conditions, about three times the usual amount of manganese was precipitated by Gibbs' method, and the precipitate was divided into approximately equal parts by pouring alternately on three filters. The precipitate in each filter was washed thirty times, 7 cc. of wash water being used each time.

The following results were obtained in two experiments.

Solubility of Precipitate. Second Series.

	In Hot Water.	In Ammonia (1:4)	In Ammonium Nitrate.
	Grams.	Grams.	Grams.
Washings contained Me- tallic Manganese. . . .	{ .0012 .0018	.0019 .0016	.0024 .0014

These results show that, if there is any preference, it is in favor of hot water.

On washing with ammonia water the precipitate is changed in color to a dark gold, which change does not occur with either of the other wash waters.

Another set of nine determinations was made in glass by boiling the solution, with constant stirring, for eight minutes, or until the precipitate seen through the walls of the beaker had a peculiar silky appearance, resembling that of mercurous chloride when precipitated from a mercuric salt by stannous chloride. The precipitate was washed with hot water.

Results of Precipitation in a Beaker and Washing with Hot Water.

	Grams.	Grams.	Grams.
Weight of Manganese Pyro- phosphate obtained . . .	{ .2450 .2445 .2440	.2445 .2443 .2443	.2450 .2445 .2442

No silica could be found in any of the precipitates after ignition. In one experiment iron was present in small amount with the manganese. The precipitated phosphate had a beautiful gold color, and on being washed with dilute ammonia dissolved gradually in the wash water, giving a brown-colored filtrate. Continued washings showed no diminution in the amount dissolved. On standing exposed to the air for several hours, a brown precipitate settled

out from the wash water. This would seem to indicate the formation of some double salt of manganese and iron, which is soluble in ammonia when an excess of an alkaline phosphate is not present.*

MASS. INSTITUTE OF TECHNOLOGY,
May, 1890.

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BY H. CARRINGTON BOLTON.

[The size is 8vo, unless otherwise stated.]

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EXPERIMENTS ON THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF THE TARTRATE OF ANTIMONY AND POTASSIUM.

BY J. H. LONG AND H. E. SAUER.

In an investigation by one of us on the polarization of solutions of potassium antimony tartrate it was observed, incidentally, that several interesting features are presented in its precipitation by other salts, notably by carbonates, phosphates, and acetates. We have made this precipitation the subject of a series of tests, the main results of which are here given.

The tartrate used for the investigation was purified by several crystallizations from the purest obtainable commercial product. An amount sufficient for all tests was prepared, powdered and preserved in uneffloresced condition in several stoppered bottles until used.

PRECIPITATION BY SODIUM CARBONATE.

When an alkaline carbonate is added to a solution of potassium antimony tartrate a precipitate is not always formed immediately. In fact, by working at a low temperature, and mixing the solutions slowly more than the total amount of carbonate necessary for complete precipitation may be added without producing even an opalescence. The polarization phenomena of such a mixture show that a chemical change of some kind has, however, taken place. When allowed to stand mixtures prepared in this way gradually become turbid, but without the escape of CO_2 , and in time a precipitate settles out. The appearance of the precipitate may be very much delayed by mixing the solutions with the least possible agitation and by keeping the mixture in a cool place.

By boiling, of course, precipitation takes place immediately, and the amount of antimony thrown down stands in relation to the amount of carbonate used.

This precipitate is referred to in the American edition of Fresenius' Qualitative Analysis as antimonious hydroxide, but the composition is not given. A precipitate having the composition $\text{Sb}_2\text{H}_4\text{O}_6$ has been analyzed by Schaffner. This corresponds to $\text{Sb}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, or $2(\text{SbOOH}) + \text{H}_2\text{O}$, containing 74.08 per cent. of antimony. In our investigations we find that the precipitate dried

at 100° has practically the composition $\text{Sb}_2\text{O}_3 \cdot \text{H}_2\text{O}$, containing 78.4 per cent. of antimony. Slight variations in the amount of water were, however, observed, and these seemed to depend on the temperature and other conditions of precipitation rather than on the temperature of drying. The amount of antimony found was occasionally greater than called for by the formula with one molecule of water.

In the first series of experiments our tests were carried out in this general manner. 5 gms. of the tartrate was dissolved in 60-70 cc. of water and cooled to 20° C. To this solution a weighed amount of sodium carbonate, dissolved in a small amount of water, was added and the mixture diluted to exactly 100 cc. at 20°. It was then allowed to stand 24 hours. Usually, in solutions containing only small amounts of carbonate, precipitation did not soon begin; in some solutions several hours elapsed, but in all cases as much precipitate as formed at all, settled out, leaving the supernatant liquid clear, before the end of the 24 hours.

When abundant enough, a portion of the precipitate was taken for analysis, and the amount of antimony left in solution was also determined. This was done by conversion into sulphide, washing and drying with the usual precautions, and weighing in a Gooch filter. The analyses of the precipitates in this series gave, in the mean 78.8 per cent. of antimony. The general results of the experiments are given in this table.

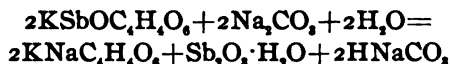
100 cc. at 20°.

No.	Amount of KSbOT.	Amount of Na_2CO_3 .	Sb_2S_3 from 50 cc.	Per cent. of KSbOT taken in solution.
1	5 gms.	.1 gm.	1.264 gm.	99.93
2	"	.3 "	1.078 "	85.22
3	"	.5 "	.890 "	70.36
4	"	.7 "	.718 "	56.76
5	"	.9 "	.517 "	40.87
6	"	1.2 "	.369 "	29.17
7	"	1.5 "	.1763 "	13.94
8	"	2.0 "	.0493 "	3.88

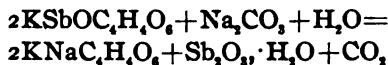
It will be seen from a consideration of the numbers of the last column how incomplete is the precipitation even with an excess of the carbonate. For the precipitation of 5 gms. of tartrate .7982

gm. of dry carbonate should be required on the assumption that 1 molecule of carbonate is sufficient for 2 of tartrate. But with these amounts, the table shows, about one-half of the antimony is still in solution. We carried out numerous parallel tests, obtaining the same general results in all cases. Exactly the same values could not be expected of course, because the extent of precipitation seems to depend, not only on the amount of carbonate and the temperature, but on the manner of mixing the solutions, and whether they are much shaken or little. As explained above, we avoided agitation as far as possible in this series of tests.

The precipitation of antimony takes place here without the liberation of CO_2 , and possibly according to this equation :



This equation is suggested by the behavior of the solutions prepared by adding the carbonate, dissolved in a definite amount of water, from a burette to solutions of the tartrate containing 5 gms. in 100 cc. The carbonate solutions had a strength of exactly 2 per cent., and when run into the tartrate solution containing a little phenol-phthalein, as indicator, nearly 80 cc. was required to give color instead of 40, which would be sufficient for this equation



From the behavior on polarization it is evident that a reaction takes place immediately on mixing the solutions. The amount of rotation is very much decreased, even without precipitation, from which it follows, apparently, that the antimony must exist in soluble form other than tartrate, as suggested by one of us elsewhere.* Something will be said below as to the form in which the antimony may be held here.

A study of the last column in the table above shows that the antimony in solution diminishes very regularly as the amount of added carbonate is increased. The extent of precipitation at this temperature is much below what is called for by theory. The next tests were made with solutions mixed at the boiling heat.

The results are given in the following table :

*Am. Jour. Sci. Oct. 1890.

100 cc. Mixed at 100° C.

No.	Amount of KSBOT.	Amount of Na ₂ CO ₃ .	Sb ₂ S ₃ from 50 cc.	Per cent. of KSBOT taken in solution.
9	5 gms.	.1 gm.	1.135 gms.	89.73
10	"	.5 "	.608 "	48.06
11	"	.8 "	.2608 "	20.61
12	"	1.0 "	.1618 "	12.80

Here the precipitation is much more complete than before. Something similar is shown in another series of tests where the solutions were mixed hot, the mixture being diluted to 100 cc. and kept in boiling water 1 hour. The supernatant liquid was filtered off and after cooling was diluted to 100 cc.

In three cases mixtures were made as before, but diluted to 250 cc. before heating 1 hour in the water bath. The results are given below.

100 cc. Kept at 100° 1 hour.

No.	Amount of KSBOT.	Amount of Na ₂ CO ₃ .	Sb ₂ S ₃ in 50 cc.	Per cent. of KSBOT taken in solution.
13	5 gms.	.2 gm.	1.002 gm.	79.23
14	"	.5 "	.5906 "	46.70
15	"	.8 "	.2751 "	21.74
16	"	1.1 "	.1095 "	8.69
17	"	1.5 "	.0802 "	6.33
18	"	2.0 "	.0560 "	4.42
19	"	3.5 "	.0591 "	4.66
20	"	5.0 "	.0600 "	4.74

250 cc. Kept at 100° 1 hour.

No.	Amount of KSBOT.	Amount of Na ₂ CO ₃ .	Sb ₂ S ₃ in 50 cc.	Per cent. of KSBOT taken in solution.
21	5 gms.	.2 gm.	.423 gm.	83.60
22	"	.8 "	.1170 "	23.12
23	"	2.0 "	.0342 "	6.76

It will be seen that the results of experiments 11, 15, and 22, are nearly the same, and also that the amount of antimony precipitated reaches a maximum, to decrease in the solutions containing the largest amounts of sodium carbonate. The excess of

this salt appears, therefore, to have a marked solvent action, increased by heat, as shown on comparing the results of experiments 18, 19, 20, and 23, with experiment 8. Precipitation seems to be least perfect in the dilute solutions as indicated by the last tests. No escape of CO_2 was observed here, while in the stronger solutions made and kept hot the loss was much less than we expected. We found .3445 gm. CO_2 in 25 cc. of the filtrate from No. 19, equivalent to 94.9 per cent. of the amount originally present, while in the filtrate of No. 20 we found 97.4 per cent. of the total CO_2 . In the strong solutions the conditions are naturally favorable for the retention of the gas.

We tried to secure more perfect precipitation in hot solutions than that shown in Ex. 18, but without much success. From considerations above, theoretically, precipitation should be completed by addition of 1.5964 gms. of the carbonate to the solution of 5 gms. of the tartrate, but a test made with these amounts showed as much antimony in solution as was left in Ex. 17, when only 1.5 gms. of the carbonate was taken. It is evident from polarization phenomena that the antimony here present does not exist as tartrate, and the increased amount with increase of added soda suggests the gradual formation of antimonite, even before a maximum in the oxide is reached.

Complete precipitation, if possible at all, must be looked for only at very low temperatures, and a study of the connection between temperature, amount of soda, and precipitation, would undoubtedly be an interesting one.

PRECIPITATION BY SODIUM ACETATE.

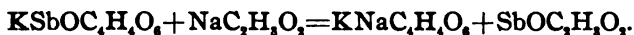
Some instructive results were obtained in a series of tests with sodium acetate. With cold dilute solutions, the precipitation is very slow, but on application of heat it becomes quite marked. In the next table are given the results found by adding to a solution of the tartrate (5 gms.) solutions of different amounts of the acetate. The mixtures were carefully made and diluted to 100 cc. at 20° , and were then allowed to stand 48 hours. In the first experiment (No. 24) only an opalescence appeared in that time, but in the other cases the mixture soon became cloudy, to precipitate and settle long before the end of the 48 hours. The clear supernatant liquids were then filtered off, the filtrate and washings

in each case being diluted to 250 cc. The antimony was determined in 50 cc., and calculated as tartrate, the results being shown in the last column.

100 cc. at 20°. Filtrate made to 250 cc.

No.	Amount of KSbOT.	Amount of NaC ₂ H ₃ O ₂ .	Sb ₂ S ₃ in 50 cc.	Percent. of KSbOT taken in Solution.
24	5 gms.	2 gm.	trace	(100)
25	"	5 "	.439 gm.	86.77
26	"	10 "	.454 "	89.72
27	"	15 "	.460 "	90.90

These numbers show that in the cold precipitation by the acetate is far from complete. It also appears that while a small amount of the acetate does not produce actual precipitation, a large excess gives less precipitation than does a much smaller amount. It is possible that the excess of acetate exerts a solvent action on antimonious hydroxide which we may look upon as precipitated in the first stage of the reaction, or it may be that a new soluble compound is formed by double decomposition in this manner:



Free acetic acid has the power of dissolving a small amount of the precipitate, Sb₂O₃·H₂O, as we found by a series of experiments. We also found that a well washed precipitate of this composition was slightly dissolved by gently warming with a solution of sodium acetate.

Acetates of antimony are scarcely mentioned in the literature, yet these experiments and others speak for their existence.

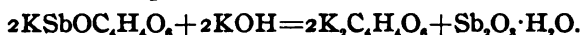
The polarization tests of the solutions of tartrate and acetate, mixed in the cold, show a steady decrease in the rotation with increase in the amount of added acetate, suggesting a progressive decomposition of the tartrate. With 2 gms. of acetate in solution only faint opalescence is produced, while with 5 gms. a marked precipitate is formed. As this precipitate decreases with further addition of acetate, it is possible that for some amount between the 2 and 5 gms. it is a maximum.

With elevation of temperature, all this is changed, however. (See table below.)

100 cc. at 100°. Filtrate made to 250 cc.

No.	Amount of KSbOT.	Amount of NaC ₂ H ₃ O ₂ .	Sb ₂ S ₃ from 50 cc.	Per cent. of KSbOT taken in solution.
28	5 gms.	2 gm.	.438 gm.	86.56
29	"	5 "	.381 "	75.30
30	"	10 "	.312 "	61.66
31	"	15 "	.291 "	57.50

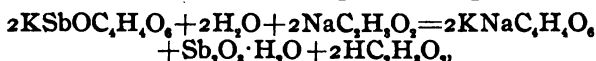
Now, 2 gms. of the acetate gives a good precipitate, and the amount of antimony thrown down from solution increases with added acetate. After heating a solution of 5 gms. of tartrate and 10 gms. of the acetate for an hour on the water bath the presence of free acetic acid was readily shown in the filtrate by titration with half normal KOH, and phenol-phthalein. No turbidity was produced in the solution until nearly 12 cc. of the alkali had been added, and the color appeared, on addition of 30 cc., as required by theory from the equation :



When alkali is added to a mixture of acetate and tartrate, prepared in the cold, a *precipitate* forms immediately and grows heavier with increase of the precipitant. Alkali, in absence of the acetate, produces a *turbidity*, but no actual precipitate at the start.

These facts seem to lead to the conclusion that at low temperatures antimony forms a stable and soluble compound with acetic acid which is decomposed with precipitation of the antimony and liberation of the acid at a higher temperature.

The 12 cc. of half normal KOH added to the filtrate from the boiled solution before an opalescence appeared, indicated that two-fifths of the tartrate had been decomposed, which corresponds closely to what is found by determination of the antimony in ex. 30. The reaction at the higher temperature is probably this :



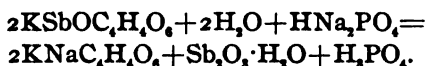
and the first alkali added simply combines with the free acetic acid. The amount subsequently added decomposes either the tartrate, $\text{KSbOC}_2\text{H}_3\text{O}_2$, in the manner indicated by an equation above, or an intermediate product, possibly $\text{SbOC}_2\text{H}_3\text{O}_2$.

The manner of precipitation strongly suggests the existence of such a product.

PRECIPITATION BY SODIUM PHOSPHATE.

Solutions of phosphates precipitate the potassium antimony tartrate in the same general manner, but the reaction appears to require a longer time for its completion. We made experiments with a number of solutions, the chief results of which are given below.

In these examples the solutions were made hot, mixed, and kept in the water-bath one hour. The filtrates obtained were strongly acid, and their behavior on titration suggested presence of free phosphoric acid, which could be liberated in this manner :



100 cc. at 100°.

No.	Amount of KSbOT.	Amount of HNa ₂ PO ₄ .	Sb ₂ S ₃ from 50 cc.	Per cent. of KSbOT taken in solution.
32	5 gms.	.2 gm.	1.234 gm.	97.56
33	"	.5 "	1.1930 "	94.32
34	"	.8 "	1.1370 "	89.89
35	"	2.0 "	.9335 "	73.77
36	"	5.0 "	.6379 "	50.43
37	"	10.0 "	.3851 "	30.52
38	"	15.0 "	.3192 "	25.24

Cold solutions can be mixed without producing precipitation, even when 1 gm. of the phosphate is present. Solutions so made were examined with the polariscope, which showed that the large rotation characteristic of the tartrate was very much diminished, probably by some decomposition in the active molecule. This behavior can be accounted for by assuming the existence of a preliminary reaction in which the antimony, in part at least, is held in an unstable form by the phosphoric acid.

It will be seen from the table that the precipitating power of the phosphate is much more marked than that of the acetate, while both fall short of the carbonate. A few tests were made with solutions of borax as a precipitant, but quantitative results were not obtained. We observed also that solutions of several other oxygen salts are unable to precipitate the antimony. This

appears to be true of sulphates, nitrates, and oxalates, at all events with solutions of moderate concentration. Cold mixtures of the tartrate with sodium hypophosphite and sodium sulphite precipitate very slowly, but if heated, decomposition begins soon. Even with sodium thiosulphate, some time elapses before a precipitate forms, which finally, after heating, appears to consist wholly of sulphide.

The reasons for these differences in behavior are not immediately apparent. The problem is complex, as we have at least four factors to deal with, viz: mass, concentration, time and temperature. It was shown by one of us by polariscopic observations* that long before a precipitate is visible in these solutions, a change has begun, and that this change is a progressive one. A solution of 5 gms. of the tartrate with .5 gm. of sodium carbonate, if carefully made and kept at a low temperature, remains perfectly clear during 24 hours, or longer; so clear that it can be examined in a polarization tube 400 mm. in length. Observations made at intervals through the 24 hours show a gradual and marked decrease in the angular rotation of the solution. Finally, a precipitate forms and separates out, but the change in the rotation, for a given temperature, is probably completed independently of this. Actual precipitation must, therefore, be preceded by a stage of preparation, which in some cases may be prolonged almost indefinitely.

As a further contribution to the subject of these precipitations, we have in mind the study of the behavior of several other salts.

CHICAGO, March, 1891.

APPARATUS FOR GAS ANALYSIS.

C. Reinhardt describes in *Stahl und Eisen* for January, 1891, the apparatus shown in the figures for analyzing the burnt gases of the Cowper stove, but which may evidently be used also for analysis of gas from other sources. The apparatus consists of two parts, that shown in fig. 1 being intended for collecting the sample, and that in fig. 2 for the analysis proper. In fig. 1, *C* is the flue leading from the stove to the chimney, *a* is an iron tube, *u* a glass flask holding $\frac{1}{2}$ to $\frac{3}{4}$ liter for collecting the sample and *m* the aspirator bottle. The bottle *m* is held in place upon the stand *k* by knees of sheet metal *o* screwed fast to it. *g* is a water reservoir from which the water flows into *m* when the latter is to be

*Loc. cit.

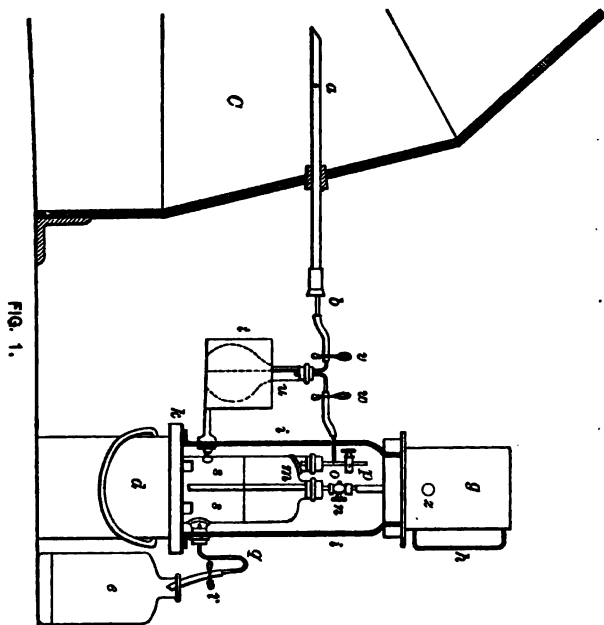


FIG. 1.

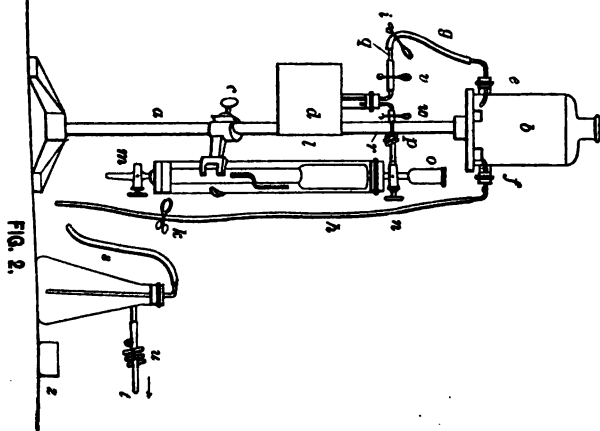


FIG. 2.

filled, and *c* a bottle into which *m* empties. For transporting the apparatus, *c* is placed inside the bucket *d* made of sheet metal, and *g* is carried by the handle *z*. *m* is filled by opening *n* and *p*; these are then closed and *v*, *w* and *r* opened when the gas is drawn over filling *w*.

The apparatus for the analysis shown in fig. 2, consists of a Bunties' burette, *l* which has a thermometer melted into one side and is surrounded by a larger tube containing water to keep the temperature as nearly uniform as possible. The burette is first filled with water by slipping the tube *h* over *m* and opening *m* and *n*, the three-way cock *n* being so adjusted that the tube communicates with *o*. The three-way cock is then fastened to the flask *d* containing the sample by means of rubber and glass tubes which (though Reinhardt does not say so) should evidently also be filled with water. The tube *g* is also filled with water, *g* is thrust into *v*, and *v*, *w* and *m* being opened, the gas flows over and fills it to a point a little below the mark. The cock *n* is then turned half way around and a little gas escapes from *o* while a little water runs in and the burette is filled exactly to the mark with the gas to be examined under atmospheric pressure. *m* is now attached to a water air pump, and a little of the water pumped out. The absorbent is then placed in *o*, the cock *n* opened and a little of the absorbent allowed to flow into the burette which is then taken out of its support and shaken to complete absorption. For absorbing the carbon dioxide, Reinhardt used caustic potash, for oxygen, alkaline pyrogallate, and for carbon monoxide, a hydrochloric acid solution of cuprous chloride.

A METHOD FOR THE DETERMINATION OF CARBON IN STEEL.

BY FRANK JULIAN.

If to a solution of steel in nitric acid, prepared as usual for the color carbon method, is added an excess of dilute solution of potassium permanganate, and the mixture digested for some hours in the cold, a precipitate of hydrated binoxide of manganese separates, which is proportional to the amount of dissolved carbon present; 36 parts carbon corresponding to 220 parts manganese. The precipitate may be separated by filtration through asbestos, and estimated by ferrous sulphate and permanganate, as usual, or otherwise.

THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINUM, IRON, BARIUM AND PHOSPHORIC ACID IN ROCK ANALYSIS.

The following method for analysis of rocks containing titanium is given by Chatard (Amer. Chem. J. 13, 106).

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, chromium, iron and aluminum, together with the phosphoric acid, are precipitated together, and, after weighing, fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides and at the same time to determine the barium, two grams of the finely pulverised mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1:1) and pure strong hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off, there should still be so much acid present as to form a solution or emulsion and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficulty-soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidize the ferrous oxide, and a little more hydrofluoric acid to insure the complete expulsion of the silica. The evaporation is then continued until the sulphuric acid fumes strongly and no odor of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

About 25 cc. of dilute hydrochloric acid (1:5) is now added, the stirring being continued, and the material is then evaporated on the water-bath until most of the hydrochloric acid has been driven off. The material is then washed into a beaker, and any residue adhering to the vessel can be removed by a few drops of hot, strong hydrochloric acid, the vessel being rubbed with a bit of paper if necessary. If the solution be very turbid it can be digested on the water-bath for some time, but ultimately it is di-

luted with hot water to 250–300 cc., allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate, and sometimes small amounts of chromite or other minerals of the same class. It is washed, ignited and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water and leached. The well-washed residue is dissolved on the filter with dilute hydrochloric acid, and this solution filtered through the same filter, which, after washing, is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute hydrochloric acid and added to the leachings, which are now acidified and added to the main solution, after reduction of the chromic acid. The hydrochloric acid solution containing the barium is evaporated to a few drops to get rid of the excess of acid, diluted, the barium precipitated, and the filtrate from the barium sulphate added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by ammonia and the precipitate redissolved by dilute hydrochloric acid. A few drops of acetic acid are added, the liquid brought to a boil, ammonia added in very slight excess, the boiling continued for a few minutes and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough, but the filtrate must be tested and the precipitation proved complete.

The precipitate is dissolved in hot dilute hydrochloric acid. The filter after washing is burned in a large platinum crucible, into which the solution, concentrated to a small bulk, is put and evaporated on the water-bath till it becomes pasty. Just enough water is now added to dissolve the salts, and then dry sodium carbonate is added in small portions, with continual stirring, till a comparatively dry mass results. This must be carefully done, for if too much soda is added at a time, and each addition is not thoroughly stirred into the mass, the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has thus been added, the mass is dried and gradually brought to a clear fusion, which should be

continued for half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete, the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes; it is then again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated, and then leached; repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute hydrochloric acid, the filter burned, the ash fused with sodium bisulphate, dissolved in water and added to the solution. The titanium in this solution is separated by the excellent method of Dr. Gooch,* all the details as laid down by him being followed. I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate, and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium the platinum generally in the solution should be removed by hydrogen sulphide.

The filtrate containing the chromic and phosphoric acids is heated, and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the aluminium phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted and the precipitate washed with a solution of ammonium nitrate until the yellow tinge disappears; it is then dissolved in dilute nitric acid, and the phosphoric acid precipitated by molybdate solution.

**Proc. Am. Acad.* 12, 435 seq. (*Bull. No. 27, U. S. G. S.*, p. 16 seq.).

The filtrate containing the chromic acid is acidified, boiled, neutralised with ammonia, and the chromium precipitated by freshly prepared ammoniac sulphide. The precipitate, after some washing, is dissolved in hot dilute nitric acid, and, after concentration, potassium chlorate is added, the solution boiled, and finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and a saturated solution of sodium bicarbonate added in small excess, separating the last traces of alumina. After standing about three hours, the alumina is filtered and washed with moderately dilute solution of the bicarbonate. The filtrate is acidified and the chromic acid reduced and precipitated by ammonium sulphide in a platinum dish, filtered, washed, redissolved to get rid of traces of alkali, reprecipitated, and finally weighed as chromic oxide.

This method, due to Baubigny for the separation of aluminum from chromium is very good and convenient if the solution be free from iron and contain but little alumina. Careful tests have shown that if iron be present some of it always remains in solution, while if there be much alumina it is almost impossible to wash out all of the chromate from the bulky precipitate with the cold solution of bicarbonate which must be used. It must also be noted in this connection that a solution of iron and chromium prepared by the Baubigny method was made ammoniacal, and it was proved that while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can safely be neglected for the purpose of shortening the work; if the whole process be carefully followed out, the results are very satisfactory, as shown by the following tests on a typical magnesium rock:

	Percentage Cr_2O_3	TiO_2	BaO	P_2O_5
No. 1270	.46	.040	.375
No. 2285	.39	.060	.385
No. 3317	.46	.055	. .
No. 4280
Average288	.44	.052	.380

The use of sodium nitrate for the fusions is not absolutely necessary, though one is more sure of complete oxidation if it be employed. In the analysis of chrome ores the best results have been obtained by fusing the finely-pulverised ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica after weighing being volatilised by hydrofluoric acid, and the residue, usually small, again fused with sodium carbonate, giving a clear solution in hydrochloric acid.

THE DETERMINATION OF WATER IN ROCK ANALYSIS.

In many cases water may be easily driven off and determined in an apparatus already described (see this Journal 4, 1), but it frequently happens that all the water is not given off unless a high temperature is attained. In such cases Chatard (*Am. Chem. J.* 13, 110) heats the rock or mineral in a platinum boat contained in a platinum tube, such as is used in making carbon determinations in iron and steel. To prevent loss by spattering when heating, as when sodium carbonate is mixed with it, the boat is enclosed in a roll of foil, one end of which is closed. To protect the platinum tube from the flame and prevent diffusion of the flame constituents into the tube, it is protected by several layers of asbestos paper soaked in saturated borax solution. The water is caught in a U tube.

E. H.

[NOTE.—Since this was written, the writer of this abstract learns that the platinum tube covered as above directed has been destroyed by the combined effect of the covering material and the high temperature.]

THE BASIC PROCESS AS APPLIED TO COPPER SMELTING.

Mr. Percy C. Gilchrist, well known in connection with the Thomas-Gilchrist basic steel process, has experimented recently upon the use of basic linings for copper refining furnaces and reports his results in a paper printed in the *Journal of the Society of Chemical Industry* (1891, Vol. X, p. 4).

The roaster furnaces have cast iron bottom plates, underneath

which a current of air circulates : by this means the bottom of the furnace is kept cool. It likewise prevents the possibility of fusion taking place between the basic hearth and its support.

The basic material used for the lining is mixed with tar in the usual way and the bottoms are formed by throwing this material into the hot furnace and burning it on in layers, beating each layer down separately and allowing it to remain exposed to the fire for several hours before adding a fresh layer. It usually takes 4 or 5 days to burn on a bottom in this way. The bottom is seasoned by melting on it some rich copper precipitate or good blister copper and absorbs about the same amount of this as would an acid lining. The tap hole is shut by throwing a little basic material against it from the inside. In other respects, except that lime is added to the charge, the working of the furnace is conducted in the usual way. The repairs are effected by addition of basic material, but are very slight in comparison with those needed with an acid lining. The best results have been obtained in the conversion of arsenical metallic bottoms, containing 5 to 7 per cent. arsenic, into blister copper. The blister copper obtained contained under 1 per cent. of arsenic and the loss of copper was 6 per cent., as against 44 per cent. in a sand lined furnace. For arsenical copper precipitates, Gilchrist therefore considers the best method to be the production of metallic bottoms which may then be treated in a basic lined furnace for the elimination of the arsenic, of course the larger the amount of arsenic contained in the bottoms, the greater will be the waste of copper in refining.

It was also found advantageous to roast white and pimple metal in the basic lined furnace, the figures obtained showing a gain of 13 per cent. in copper saved.

In the refining furnace the gain was less, but the author thinks that it is to be preferred to an acid lined furnace, notwithstanding the slightly greater first cost of the basic lining. Comparative results show that while it is quite possible to refine impure arsenical copper in an acid lined furnace the loss of copper is less for the same degree of purity with a basic lining, except where antimony and bismuth must be slagged off; in this case acid lining seems to be preferable.

THE OILS AND FATS.

Behavior of the Fatty Acids when Heated.—(R. Tatlock J. Soc. Chem. Ind. Apr. 1890). When the acids from olive oil are heated at 90° C. for 720 hours they lose in weight to the extent of about 7½ per cent. The acids from Castor oil lose on heating for 120 hours at 90° C. 3.18 per cent. The acids from cotton-seed oil under the same conditions lose 2.13 per cent. The linseed oil acids gained 0.19 per cent. Stearic acid lost 1.78 per cent.; the acids from olive oil containing 9.42 per cent. free oleic acid gained 0.10 per cent. and when the free fatty acid was removed, 0.36 per cent.

In the discussion which ensued it was suggested that perhaps this loss was due to an excess of hydrochloric or sulphuric acid which remained entangled with the fatty acid and gradually volatilized. To this suggestion Mr. Tatlock replied that but a very slight excess of hydrochloric acid had been added, less excess having been used than the amount lost. The saponification had been effected by alcoholic potash and the glycerine must have been washed out, so that the loss could not have arisen in this way.

E. H.

Wool-Fat and Methods for Obtaining It.—(H. W. Langbeck, J. Soc. Chem. Ind. Apr. 1890.) The wool is washed with water and the solution concentrated in a Yaryan quadruple effect apparatus to extract the potash salts contained in it. The wool is then washed and scoured with a soap lye, consisting of an emulsion of olive oil and potash lye, diluted with water. This extracts all the fat together with the remaining dirt. The emulsion obtained is evaporated in a Yaryan and the wool is washed with water, pressed and dried. The evaporated emulsion is treated with a mixture of methylated alcohol and water which dissolves out the soap, while the wool-fat is insoluble. The wool-fat is separated from the dirt either by hot pressing or by solution in benzine or carbon disulphide. This wool-fat is further purified by filtration through that form of animal charcoal known as prussiate waste. This may be done either by melting the fat and filtering hot or by dissolving in benzine and filtering the solution. The purified fat has a yellow color. If required as a basis for

ointments, etc., it is incorporated with 20 to 30 per cent. water or solution of hydrogen dioxide, thus producing a pure white material. The wool-fat consists principally of ethers of cholesterine and ischolesterine. It contains free cholesterine and perhaps other unsaponifiable material, and consequently cannot be used in soap and candle making.

E. H.

Examination of Oils, Fats, and Allied Substances.—Thomas T. P. B. Warren, Chem. News 62, 288. For obtaining the specific gravities of oils, the author has designed a specific gravity bottle, holding 25 cc. to the neck which is graduated and widened at the top into a funnel. The capacity of the bottle and graduated neck are determined by pure mercury, so that the expansion due to the glass itself can be accurately measured and allowed for if required. The mercury is preferably distilled direct into the bottle, otherwise it is not easy to expel the air. In using this bottle, it is immersed in water or oil to the upper mark of the neck, while a platinum wire serves to suspend it while weighing or holding in an oil or water-bath. The capacity of the bottle being known, the specific gravity of an oil occupying the same bulk is easily determined. The expansion of an oil, the writer points out, is in a geometrical ratio. Oils easily oxidized are best heated in a flask with a bent neck dipping under mercury, or in connection with a vacuum pump. If the rate at which an oil absorbs oxygen is required, a measured volume of the gas contained in a graduated gas tube with an outlet at the top, standing over mercury, is connected with a flask containing the oil, the air in which has been displaced by oxygen, and the volume noted. The residual gas in the tube is analyzed. The carbonic acid represents approximately the glycerine set free, and the deficiency of oxygen beyond this shows what the oils and fatty acids have retained.

A. H. W.

The Alcohol Test for Pure Castor Oil.—J. Arthur Wilson, Chem. News 62, 215. For carrying out this test, one measure of the castor oil is mixed thoroughly with two volumes of spirit of exactly 0.838 sp. gr., and then heated, stirring well with a thermometer, until complete solution takes place. For the case of genuine castor oil, this will be between 38° and 43°C., while the

presence of any foreign oil prevents solution until a much higher temperature is reached.

A. H. W.

On the Chemical Composition of the Oils of Wintergreen and Birch and the Characters of the Synthetic Oil of Wintergreen.—Frederic B. Power, Chem. News **62**, 67, 75 and 91.

I. Natural Oil of Wintergreen.—400 gms. were decomposed by heating on a water bath for about two hours in a flask with an inverted condenser, with a solution of 200 gms. caustic potash. The liquid was then diluted with water and distilled until oil ceased coming over, and a redistillation of the distillate was afterwards made, in order to bring the drops of oil or the terpene within a smaller compass and more readily separate it from water. The isolated terpene was a somewhat viscid yellowish liquid, with a marked pepper-like odor as described by Cahours, and a specific gravity of about 0.94. Vapor density determinations were undertaken, but without satisfactory results. The strongly alkaline liquid remaining in the flask after the distillation of the terpene was subsequently shaken with ether, but the latter on evaporation yielded only a small amount of a dark colored resinous substance. The salicylic acid was separated from the alkaline liquid by means of hydrochloric acid, and after being collected on a strainer and washed, was crystallized from boiling water.

II. Natural Oil of Birch.—300 gms. of this oil were treated in a similar manner to the oil of wintergreen. After saponifying, a considerable amount of a light liquid was observed on the surface of the alkaline mixture, which was removed as carefully as possible with a pipette and placed in contact with freshly ignited potassium carbonate. The alkaline liquid in the flask was then further diluted with water and distilled to remove the remaining portion of the hydrocarbon. On shaking the alkaline mixture with ether, and allowing the latter to evaporate, a dark colored resinous mass was obtained, as in the case of oil of wintergreen. The liquid separated from the oil of birch amounted to 13.5 gms. or 4.5 per cent., so probably 5 per cent. was present in the first place. Its specific gravity was 0.8066 at 15°, and it was found to have no constant boiling point. Analysis of the portion distilling below 270°, gave the following results:

	I.	II.
C	80.45 per cent.	81.37 per cent.
H	13.63 "	13.49 "
	<hr/> 94.08 "	<hr/> 94.86 "

from which the inference was drawn that the liquid was a mixture of hydrocarbons, containing some oxygenated bodies, and a further examination revealed the presence of kerosene oil, evidently used as an adulterant in this case. An ultimate analysis of pure oil of birch gave :

	$C_6H_6O_2$ Calculated.	Found
C	62.16	62.80
H	5.26	5.32
O	31.58	31.88
	<hr/> 100.00	<hr/> 100.00

confirming the author's theory that natural oil of birch consists of pure methyl salicylate. After the separation of the petroleum from the oil of birch, the alkaline mixture was treated with hydrochloric acid and the salicylic acid thus obtained.

III. Artificial or Synthetic Oil of Wintergreen.—The author examined the artificial oil for the detection of benzoic acid, which has been said to be present, but found no traces. The conclusions deduced from these investigations are :

1. The natural oil of wintergreen consists of methyl salicylate with small amounts (0.3 per cent. or less) of a terpene, and the latter does not solidify or separate any solid substance at a temperature of -10°C . Oil of wintergreen deviates the ray of polarized light to the left and cannot be vaporized without decomposition.
2. The oil of birch when pure consists of methyl salicylate, and is without action on polarized light.
3. The natural oils of wintergreen and birch are, therefore, neither physically nor chemically identical, although the differences are practically very slight.

A. H. W.

Examination of Oils, Fats and Allied Substances.—Thos. T. P. Bruce Warren, Chem. News 62, 215. The author gives the following equation for dealing with a mixture of two oils—linseed

and lard, for example. The iodine absorption per cent. of the former is 170, of the latter 52.5, and x and y are the quantities respectively of each oil required to give an iodine absorption of 84.5 per cent.

$$(170 \times x) + (52.5 \times y) = 84.5 (x + y)$$

$$170x - 84.5x = 82.5y - 52.5y.$$

$85.5x = 32y$, or 117.5 parts of the mixture contains $85.5 \times x$ and $32 \times y$ of the separate oils. Make $y = 1$, then the question is how much lard oil = 52.5 per cent. must be mixed with 1 part linseed oil = 170 per cent, to yield a mixture = 84.5 per cent. iodine absorption.

$$\frac{170 + 52.5x}{x + 1} = 84.5 \text{ whence } x = 2.67, \text{ i. e., 1 part of linseed oil}$$

and 2.67 parts lard oil is the mixture required, for

$$52.5 \times 2.67 = 140.17 \text{ lard oil,}$$

$$\frac{170 \times 1.00}{3.67} = \frac{170.00}{310.17} \text{ linseed oil.}$$

$$\frac{310.17}{3.67} = 85.5, \text{ the iodine absorption required; then}$$

$$3.67 : 2.67 :: 100 : 72.8 = \text{per cent. lard oil.}$$

$$3.67 : 1.00 :: 100 : 27.2 = \text{per cent. linseed oil, and}$$

$$72.8 \times \frac{52.5}{100} = 38.22, \text{ iodine absorption for lard oil; and}$$

$$27.3 \times \frac{170}{100} = 46.41, \text{ iodine absorption for linseed oil.}$$

$$84.63, \text{ iodine absorption of mixture.}$$

The numbers for the iodine absorption of each oil, if subtracted from the averages of the iodine absorption of the mixture and 100, will give the percentage quantity of each oil. With more

than two oils, other functional equations are necessary for correct results. Let $M=100$ be a mixture of olive, lard, and linseed oils, with iodine absorptions 84.5, 52.5, and 170 per cent. respectively, and let 84.5 be the iodine absorption of M . Let 58.5°C . be the rise of temperature (Maumené's reaction) observed on M , and 42° , 42° , and 133°C . be the rise of temperature noted on each oil respectively. Let x , y and z be the unknown quantities of each oil. Then

$$(1) \quad x + y + z = M = 100.$$

$$(2) \quad 100 \times 84.5 = 84.5x + 52.5y + 170z.$$

$$(3) \quad 100 \times 58.5^{\circ} = 42^{\circ}x + 42^{\circ}y + 133z.$$

Combining (1) and (3)

$$42(x + y) + 133z = 58.5 \{ (x + y) + z \}$$

$$x + y = 4.51z. \quad \text{Substituting in (1)}$$

$$4.51z + z = 100, \text{ whence } z = 18.1 \text{ per cent. linseed oil.}$$

$$(4) \quad x + y = 100 - 18.1 = 81.9 \text{ per cent. olive and lard oils.}$$

From (2)

$$84.5x + 52.5y + (170 \times 18.1) = 8450.$$

Subtracting 170×18.1 from each side

$$(5) \quad 84.5x + 52.5y = 5373.$$

From equation (4) $y = 81.9 - x$. Substitute this value in (5).

$$32x = 1057.2; \text{ or } x = 33.00 \text{ per cent. olive oil and}$$

$$81.9 - 33.0 = 48.9 \text{ per cent. lard oil.}$$

Summarizing :

Olive oil	=	33.00 I. abs.	27.88
Lard "	=	48.90 "	25.67
Lins'd "	=	18.10 "	30.77
		<hr/>	<hr/>
		100.00	84.32

Actual Mixture :

Olive oil	33.30
Lard oil	48.50
Linseed oil	18.10
	<hr/>
	100.00

A. H. W.

Examination of Oils, Fats and Allied Substances.—Thomas T. P. Bruce Warren, Chem. News **62**, 251. In the following list of oils, those in the first division yield insoluble products with sulphur chloride, those in the second do not yield such products. The first division oils when heated strongly with sulphur yield spongy elastic masses, except the oils of olive and cotton-seed. The sulphur which they dissolve separates out on cooling. All dissolve in ether, but, on adding a few drops of alcohol, caoutchouc and gutta-percha separate out.

First Division.

Olive oil.	Walnut decort.
Olive oil from Green Olives.	Sesame.
Olive oil from kernels of Green Olives.	Niger seed.
Poppy Oil, var.:	Castor oil.
Papav. somnif.	Rape seed.
Glaucium flav.	Rape seed, blown.
Almond, var.:	Cotton-oil.
Amygd. dulc.	Cotton-oil, crude.
Amygd. amar.	Cotton-oil, blown.
Earthnut.	Beechmast.
Earthnut decort.	Hemp seed.
Caoutchouc, gutta-perch and allied substances,	} and the resins naturally associated with them.

Second Division.

Petroleum and Homologues of the Paraffin Series, Distillates from Coal Tar, Shale, and Similar Minerals.

Sperm Oil.	Beef-fat.
Whale Oil.	Mutton-fat.
Cod Oil.	Cocoa-nut oil.
Spermaceti.	Palm Oil.
Lard.	Resin Oil.
Lard Oil.	Pine Resin.
Butter.	Turpentine.
Bees-wax.	Japan Wax.

Glycerin and the fatty acids of the first division must be included in the second class. By treating a mixture with ozonized oxygen, an easily oxidized oil can be separated from one not so readily acted upon. When treating with nitric acid, it should be borne

in mind that a few drops of nitro-glycerine are formed, which should be removed before subsequent treatment. Petroleum and the distillates from coal-tar act simply as solvents of sulphur chloride.

A. H. W.

SEPARATION OF BARIUM, STRONTIUM AND CALCIUM.

A. Russman, Chem. News **63**, 13 and 44. (Ztschr. für anal. Chem.) The author has prepared an exhaustive memoir, on a critical examination of different methods employed for separating these three allied elements.

1. *Method of Frerichs*, precipitation as chromates, after addition of acetic acid and ammonium acetate. For separation of barium and strontium, it was found that in solutions which contain from 10 to 15 parts of strontium to 50 parts of barium, no strontium is precipitated, but where the proportion of strontium present is in excess of these figures, appreciable quantities of strontium chromate are brought down with the barium salt, but calcium chromate is not precipitated. The endeavor to determine barium volumetrically, by decomposing the barium chromate with hydrochloric acid and potassium iodide gave too high results. The best course was found to be dissolving the barium chromate in dilute hydrochloric acid, adding potassium iodide, and titrating immediately after dilution with sodium thiosulphate.

2. *C. Diehl's Method*.—(Journ. Prak. Chemie.) Freshly precipitated barium and calcium sulphates were gently heated with a concentrated solution of sodium thiosulphate, which dissolves the calcium but not the barium salt. Not found satisfactory, since the barium sulphate retains some of the calcium, the error being greater as the proportion of calcium present is larger. In order to determine the calcium in the filtrate, it is also necessary to decompose the sodium thiosulphate by boiling, which leads to another source of error, since the sulphur is apt to enclose small quantities of the calcium salt.

3. *Separation of Barium and Calcium by Means of H_2SO_4* .—Successfully employed in solutions containing small quantities of

barium with a large amount of calcium or those containing one part calcium with 100 parts barium. If 10 to 20 cc. hydrochloric acid, containing 25.28 per cent. HCl, are used, no calcium is precipitated with the barium, but in very dilute solutions, twenty-four hours are needed for complete precipitation.

4. *Method of D. Sidersky.*—A neutral solution of strontium and calcium compounds is boiled with a mixture of ammonium sulphate and oxalate. If there is at least 8.4266 per cent. of hydrochloric acid present in the solution before precipitation, thus holding the calcium in solution, approximate results may be obtained, and the method may be also applied to the separation of barium and calcium.

5. *C. H. Bloxam's Method.*—(See Chem. News 54, 16 and 168.) In criticising this method, Russman concludes it is well adapted for the detection of small quantities of calcium in presence of much strontium, but the determination of calcium by means of ammonia and arsenic is far more difficult than by means of the oxalate precipitate, and it was found impossible to avoid loss of arsenic on attempting to ignite the precipitate, for weighing as $\text{Ca}_2\text{As}_2\text{O}_7$. The method cannot be used for the quantitative separation of strontium and calcium with any reliability.

6. *E. Fleischer's Method.*—The precipitated carbonates of barium, strontium, and calcium are dissolved in a measured quantity of hydrochloric acid of known strength, the excess of acid is determined by titration, the barium is precipitated with potassium chromate from the neutralized solution, and the barium chromate is determined volumetrically with ferrous sulphate. The proportion of calcium and strontium is calculated from the amount of barium found, and the quantity of hydrochloric acid consumed in dissolving the weighed carbonates, after deducting the proportions belonging to the barium. The volumetric determination of the barium gave results too low. The process followed consisted in dissolving the washed precipitate of barium chromate in hydrochloric acid, precipitating as sulphate, titrating the filtrate with ferrous sulphate, and using permanganate for determining the excess.

Where only barium and calcium are to be determined, in the

absence of magnesium, Fleischer converts the barium into sulphate and the calcium into carbonate, by digesting the solution of both with a mixture of three parts potassium sulphate and one part potassium carbonate, drying and igniting the precipitate and determining the calcium volumetrically. Russman found this method to be successful.

7. *Method of W. G. Levison.*—W. Gibbs having shown that some metals may be determined by precipitating their sulphates, nitrates, or chlorides in a concentrated solution with oxalic acid and strong alcohol, and determining the oxalic acid in the precipitate by titration with permanganate, alkaline salts, of course, being absent. Levison has applied this method to the determination of barium strontium and calcium. Hot hydrochloric or dilute sulphuric is used for the decomposition of the oxalates. In the latter case, it is necessary to filter through sand, since sulphuric acid dissolves out matter from the filter paper capable of acting upon permanganate. Barium oxalate cannot be completely decomposed by sulphuric acid, but with calcium and strontium determinations Russman obtained good results with this method.

A. H. W.

DETERMINATION OF ALUMINUM IN STEEL AND PIG IRON.

M. Carnot states that the method is very similar to that published by Mr. J. E. Stead in the *Journal of the Society of Chemical Industry*, 1889, p. 965, but that he has used and taught it at the *Ecole des Mines* for eight years. It is founded on the reaction that he pointed out in 1881, that aluminum is precipitated as the neutral phosphate $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ from a boiling solution faintly acid with acetic acid. The precipitation succeeds equally well when the solution contains iron, if the ferric salt has been previously reduced to ferrous, by hyposulphite of soda.

Treat 10 gms. of the iron or steel in a platinum dish covered with a piece of platinum foil, with hydrochloric acid, and when solution is complete, dilute and filter into a flask, washing the carbon, silica, etc., on the filter, thoroughly with distilled water.

Neutralize the solution with ammonia and carbonate of soda, but see that no permanent precipitate is formed, then add a little hyposulphite of soda, and when the liquid, at first violet, becomes colorless, 2 or 3 cc. of a saturated solution of phosphate of soda and 5 or 6 gms. of acetate of soda dissolved in a little water. Boil the solution for about three-quarters of an hour, or until it no longer smells of sulphurous acid. Filter and wash the precipitate of phosphate of alumina mixed with a little silica and ferric phosphate, with boiling water. Treat the precipitate on the filter with hot dilute hydrochloric acid, allow the solution to run into a platinum dish, evaporate to dryness, and heat at 100° for an hour to render the silica insoluble. Dissolve in hot dilute hydrochloric acid, filter from the silica, dilute to about 100 cc. with cold water, neutralize as before, add a little hyposulphite in the cold, then a mixture of 2 gms. of hyposulphite and 2 gms. of acetate of soda, boil until all smell of sulphurous acid has disappeared, filter, wash, and weigh as $Al_2O_3P_2O_5$, which contains 22.18 per cent. of aluminum. (A. Carnot, *Moniteur Scientifique*, 1891, p. 14.)

A. A. B.

NOTES.

Food Preservation.—Dr. C. A. Crampton, President of the Chemical Society of Washington, recently delivered an interesting address before that society on "Food Preservation and Food Preservatives." He gave special attention to the use of chemicals as preservative agents, and quoted the most reliable tests for their detection in foods. The address has been published in pamphlet form.

S. C.

The Aluminum Problem.—In a lecture delivered before the Franklin Institute January 12, 1891, and reprinted in the *Journal of the Franklin Institute* for March, J. W. Richards sketches the history of aluminum and compares the present processes for its manufacture. He thinks it not improbable that by dissolving alumina in some solvent, and submitting it to the action of carbon at a temperature within the range of ordinary blast furnace work, it may be found possible to reduce aluminum more cheaply than by the present electrical methods.

E. H.

An editorial in the *Chemical News* (61, 195), under the head of "Analytical Touts," adverts to the case of a person who called himself an "F. C. S.," and sent advertisements to manufacturers offering to analyze their products for the sake of using the analysis as a business card. The Chemical Society, unlike the professional organizations, the Pharmaceutical Society for instance, has no redress at present in case a person falsely assumes the title of Fellow.

A. H. W.

Obituary: On February 21, at Helena, Montana, Francis Clark Blake, in his thirty-eighth year. Mr. Blake was born in 1853, and was educated at the Worcester Free Institute of Industrial Science. After graduation, he came to Lafayette College as an Instructor in Chemistry. He was then employed by the Pennsylvania Lead Company, shortly became their superintendent, and has served them in that capacity for ten years. He married a daughter of Dr. A. A. Ballard, Professor of Moral Philosophy and Rhetoric in Lafayette College. His wife, with three children, survives him. Mr. Blake's work was largely in industrial lines, but he was a great student, a clear thinker, and a man of broad and liberal views. He improved the English cupellation hearth,* introduced into the works of his company electrolytic processes for the purification of silver and gold, improved the method for manufacturing cupels, and wrote several other papers upon subjects connected with his work.† He was a man of fine presence and lovable personal qualities.

E. H.

**Trans. A. I. M. E.*, X, 220.

†See this *Journal* 1, 224; 2, 71, 250, 405; *Trans. A. I. M. E.* 9, 316; 10, 220, 490; 15, 657, 661.

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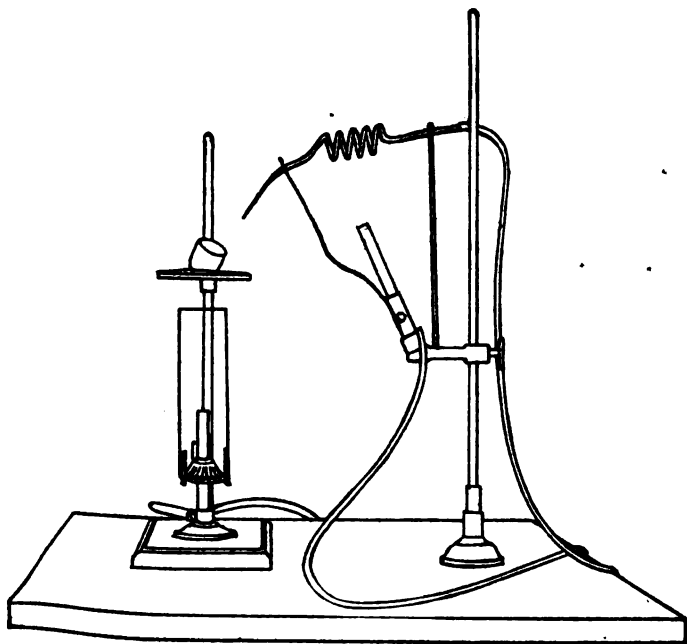
APPARATUS FOR HASTENING EVAPORATIONS.

BY J. EDWARD WHITFIELD.

It is very well known that in dissolving siliceous residues in hydrofluoric and sulphuric acids and evaporating to dryness, or in treating the insoluble portion of ores in the same way to get rid of the silica, the contents of the crucible are very liable to spatter unless the heat used is very low, and this naturally causes the operation to be somewhat lengthy.

Having frequently to make use of this method, the piece of apparatus shown in the figure was devised to hinder as much as possible the spattering and to shorten the time of evaporation.

A platinum tube of about 3-16 in. external diameter is coiled



and supported above a burner as shown in the figure. After the burner has been lighted long enough to heat the spiral part of the tube red hot, air is driven through it and directed into the crucible. By having both the burner and spiral mounted on a movable arm it is a very simple matter to so adjust it as to get the best effects of the hot blast.

This arrangement answers very well in hastening the evaporation of liquids from beakers while on the sand or air-bath, if care is taken that the beaker is hot before the hot blast is directed against its sides. A spiral tube is not altogether essential to the apparatus, but as the spiral represents more surface than a straight tube the temperature of the blast is proportionally higher. A cold blast directed into the crucible will prevent spattering, but the evaporation will necessarily be slower.

In the laboratories connected with ironworks, where a blast is always available, this apparatus can be made use of to great advantage, and in general laboratories a blast of air sufficient for ordinary work can be gotten from a small Wigmore blower and a $\frac{1}{8}$ H. P. electric motor supplied with power from the lighting service or from a battery.

LABORATORY OF BOOTH, GARRETT & BLAIR,
PHILADELPHIA, PA.

DETERMINATION OF CARBON IN STEEL.

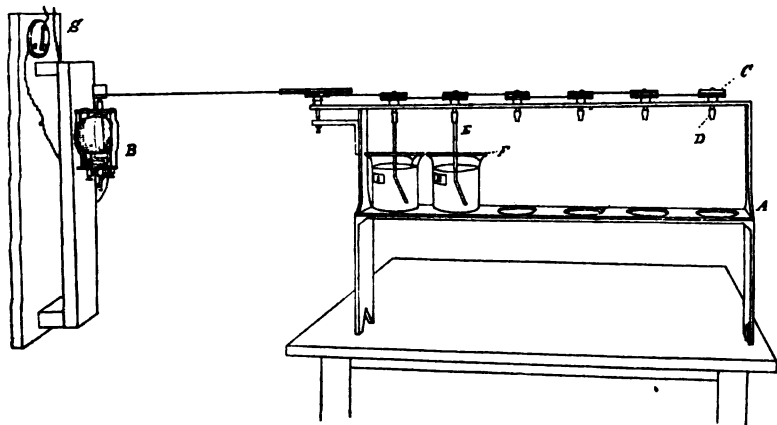
A STIRRING MACHINE FOR FACILITATING THE SOLUTION OF STEEL IN THE DOUBLE CHLORIDE.

By A. A. BLAIR.

The most tedious part of the determination of carbon in steel is frequently that which has to do with the decomposition of the steel and the solution of the precipitated copper. This is particularly the case with low steels, as the samples are nearly always in lumps and the analyst does not like to separate these larger particles for fear that the fine stuff alone may not represent a true average. To shorten the time required for this part of the operation and at the same time to avoid the labor of stirring by hand, I had the machine shown in the cut constructed. It consists of a framework *A* of brass, cast in one piece for the sake of rigidity. It is fastened to the table by lugs and screws not shown in the cut. The shelf, on which the beakers stand, has on it a piece of

asbestos board with holes to fit exactly the bottoms of the beakers, to prevent them from moving. To further increase the stability of the beakers (which should be of very heavy glass) their bottoms are ground on a glass plate with fine emery until they have a good bearing surface all around.

The tops, which are covered when on the machine with a plate of glass *F* ground on one side and perforated to allow the passage of the stirring rods *E*, are likewise ground, so that when



slightly moistened the ground glass surfaces prevent almost entirely all movement of the cover on the beakers, when the machine is in motion.

The small wooden pulleys *C* are fitted with brass spindles which run through the upper cross piece and have on their lower ends pieces of rubber tubing *D*, which serve to hold the stirring rods. The stirring rods are bent as shown in the cut to give the proper motion to the liquid. A small motor *B* adapted to the strength of the current furnishes the requisite power. The motor if properly wound may be attached to an ordinary incandescent lighting current, as I now use it, but a sewing machine motor run by a dipping battery of three bichromate cells is sufficient to give the necessary number of revolutions. I used the latter arrangement for three years and have had the machine in constant use for about four years, during which time it has been perfectly satisfactory in every respect.

LABORATORY OF BOOTH, GARRETT & BLAIR,
PHILADELPHIA.

THE ELECTROLYTIC ASSAY OF COPPER.

BY STUART CROSSDALE.

[Continued from page 140.]

SEPARATION OF COPPER FROM OTHER METALS.

In the following experiments only those metals have been used that are commonly associated with copper, and they have been added in such quantities that they will represent, for the most part, extreme cases. No attempt was made to work rapidly. Several assays were started in the afternoon and allowed to run over night. The next morning they were ready to weigh. The strength of the current was from 0.3 cc. to 0.5 cc. OH gas per minute, unless stated otherwise. This deposited the copper in a firmly adherent and bright metallic coating, that could be easily washed, and that did not oxidize when exposed, for a long time, to the atmosphere.

COPPER FROM ALUMINUM.

These metals can be readily separated from each other by electrolysis in nitric (Luckow), sulphuric, and phosphoric acid (Smith) solutions; and also from a solution of the double alkaline oxalate (Classen.).

Both metals were present as sulphates. The aluminum equaled 300 per cent. of the copper.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(17)	0.0738	2	50	0.0738	. . .
(18)	0.0719	2	50	0.0720	+ .0001
(19)	0.0719	2	50	0.0719	. . .
(20)	0.0730	2	50	0.0728	— .0002
(21)	0.0728	1	50	0.0726	— .0002
(22)	0.0713	1	50	0.0711	— .0002
(23)	0.0680	0.5	50	0.0681	+ .0001

No. 23 was the only one washed with the current running. Nos. 20, 21 and 22 showed traces of copper in filtrates.

COPPER FROM ANTIMONY.

Antimony is deposited to some extent with the copper, but satisfactory determinations can be made from an acid solution when the former does not exceed one-third the weight of the latter (Wrightson). The separation cannot be made in a solution of

the double oxalate except when antimony is present in small quantities (Classen). Antimony forms a dark coating on the electrode after the greater part of the copper has been deposited. When the deposit of antimony is small, the copper may be determined by igniting the electrode; this will volatilize the antimony and oxidize the copper. The latter is then dissolved and reprecipitated by electrolysis (Directors Mansfield Copper Works).

Preliminary separations can be made by treating with sodium sulphide; or by repeated evaporation with nitric acid.

In the first experiments the antimony was converted into the sulphate and then treated with water to form a solution that would be of the same strength as that of the assay. The basic salt was allowed to settle, and a measured quantity of the clear solution was drawn off for each assay. The amount of antimony in this solution was not determined.

The following results show that copper may be separated from antimony by electrolysis when the latter is present in very small quantities. The strength of the current should not exceed 0.3 cc. to 0.4 cc. OH gas per minute, and the assay should be removed from the circuit soon after the precipitation of copper is complete.

No.	Copper Used.	Free H ₂ SO ₄ .	Total Solution.	Copper Found.	Difference in Weight.	Copper Reprecipitated Alone.
	Gm.	cc.	cc.	Gm.	Gm.	Gm.
(24)	.0680	1	60	.0677	— .0003	.0675
(25)	.0706	1	60	.0704	— .0002	.0703
(26)	.1368	0.5	50	.1369	+ .0001	.1368
(27)	.1014	0.5	50	.1013	— .0001	.1011
(28)	.1149	0.5	50	.1050	+ .0001	.1148

The filtrate from the reprecipitated copper in No. 28 gave a slight test for antimony. The filtrates from the others were not examined. The next series of experiments were made to determine whether the copper could be completely removed from the antimony or not when the latter was precipitated as a basic salt or as the pentoxide. In both cases the separation was incomplete, and no satisfactory results were obtained. The only method for a complete separation seems to be that by which the sulphides of the metals are treated with sodium sulphide. This dissolves the antimony and leaves the copper sulphide unattacked. The latter is then dissolved in acid and submitted to electrolysis.

COPPER FROM ARSENIC.

Arsenic is not deposited from a sulphuric or nitric acid solution containing arsenious acid equal to 50 per cent. of the copper, so long as an insoluble anode is used (Eustis). It is not deposited until after the copper is all precipitated, and at that point the current must be stopped (Ohl). "Arsenic precipitates partly *with* the copper, and not *after* it, as has been supposed (Torrey & Eaton). Copper cannot be separated from arsenic in an acid solution (Luckow) when the latter exceeds 0.2 per cent. of the former (Classen). The same results are obtained from a solution of the double oxalate (Classen).

The separation can be made in a solution of potassium cyanide (Smith and Frankel), and in an ammoniacal solution containing potassium arsenite (McCay*). Arsenic is deposited as a black coating, and when present in small quantities, it may be separated from the copper by volatilization; the latter is then determined by dissolving and reprecipitating (Directors Mansfield Copper Works).

Preliminary separations can be made by treating the precipitated sulphides with sodium sulphide; by evaporating with bromine in a hydrochloric acid solution (Classen); and by reducing to arsenious acid and evaporating to dryness with strong hydrochloric acid (Campbell,† McIntosh‡).

In this laboratory arsenic was found to be deposited from a sulphuric acid solution when present in quantities of less than 1 per cent. of the copper. Assays were made containing as much as 2 cc. free H_2SO_4 in a total solution of 50 cc., and with a current as low as 0.2 cc. OH gas per minute, but the precipitation of the copper was too slow under these conditions. The following results were obtained with 1 per cent. arsenic:

No.	Copper Used. Gm.	Free H_2SO_4 . cc.	Total Solution. cc.	Strength of Current. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(29)	.1496	2	50	0.3	.1491	— .0005
(30)	.1294	2	50	0.3	.1300	+ .0006

Both copper precipitates were stained with arsenic, although the precipitation of copper in No. 29 was incomplete. This, as

*Chem. Zeit. 14, 509; J. Soc. Chem. Ind. 9, 822; this Journal 4, 459.

†This Journal 2, 370.

‡This Journal 1, 390.

well as other experiments which are not given here, confirms the statement of Torrey & Eaton that arsenic is deposited with the copper near the end of the precipitation and not after it. Efforts were made to remove the arsenic by evaporation with bromine and hydrochloric acid, as directed by Classen, but they were unsuccessful. Oxalic acid and alcohol were then tried as reducing agents, but repeated evaporations in a beaker with concentrated hydrochloric acid failed to remove all the arsenic. The former, however, was not used in as large quantities as directed by Campbell, and perhaps was not fairly tested. Ammonium bisulphite was substituted as a reducing agent, and the evaporation was made in a small flask provided with a cork and tube. Nos. 31 and 32 were evaporated four times with the addition of 20 to 30 drops of bisulphite at each renewal of the acid. No. 33 was evaporated three times. No arsenic was deposited with the copper and no copper was left in the filtrates. No. 32 must have sustained some loss during the manipulation.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(31)0465	1	50	.0465	. . .
(32)0411	1	50	.0407	— .0004
(33)0476	1	50	.0475	— .0001

COPPER FROM BARIUM.

This separation is easily made in a nitric acid solution (Luckow, Classen). In the presence of sulphuric acid the barium is completely separated as sulphate, which must be filtered off.

No.	Copper Used. Gms.	Free H ₂ SO ₄ . cc.	Total Solution. Gms.	Copper Found. Gms.	Difference in Weight. Gms.
(34)1012	0.5	50	.1012	. . .
(35)1018	0.5	50	.1018	. . .
(36)0675	0.5	40	.0674	— .0001
(37)0703	0.5	40	.0703	. . .

COPPER FROM BISMUTH.

These metals cannot be separated in an acid solution (Luckow, Stillman, Torrey & Eaton, Stahl), nor in a solution of the double oxalates (Classen).

The separation can be made in an alkaline solution of the citrate containing an excess of potassium cyanide (Smith & Frankel).

Preliminary separation must be made for the electrolysis of an acid solution by precipitating the bismuth twice as a basic chloride (Stahl).

Bismuth was found to be easily deposited, and came down with the copper when present in any amount. Separation from the latter as a basic salt proved to be incomplete and difficult to work. They were, however, readily separated by means of ammonia in a nitric acid solution as described by Rose.* Two precipitations of the bismuth were made in experiments 39 and 40. In No. 38 the bismuth was precipitated three times. The final washing in each assay was done with water containing a little ammonia. The precipitated copper apparently contained traces of bismuth that had been redissolved by the excess of ammonia; and the bismuth hydroxide seems to retain traces of copper even after the second or third precipitation. The error is probably not enough to interfere with practical work, but with very small quantities of bismuth, the method must be inaccurate.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(38)0501	0.5-1	50	.0496	— .0005
(39)0475	0.5-1	50	.0475	. . .
(40)0465	0.5-1	50	.0466	+ .0001

The filtrates contained no copper.

COPPER FROM CADMIUM.

Copper may be separated from cadmium in a nitric (Smith†), in a sulphuric (Smith & Frankel, Boisbaudran), and in a phosphoric acid solution (Smith). The separation cannot be made in a solution of the double oxalates (Classen).

The following experiments confirm the work of Smith & Frankel. The strength of the current should not exceed 0.3 cc. OH gas a minute. During the first five minutes of these assays the current measured nearly 0.4 cc. gas a minute, which is probably the cause of the high results. The filtrates contained no copper.

*Pogg. Annal. 110, 430.

†Am. Chem. Jour. 2, 42.

No.	Copper Used. Gms.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gms.	Difference in Weight. Gms.
(41)0832	1	50	.0834	+.0002
(42)0812	1	50	.0814	+.0002
(43)0832	1	50	.0833	+.0001

COPPER FROM CALCIUM.

These metals are easily separated in a nitric acid solution (Luckow, Classen). In the presence of sulphuric acid the calcium is precipitated as sulphate, and must be filtered off.

No.	Copper Used. Gms.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gms.	Difference in Weight. Gms.
(44)1075	0.5	50	.1075	. . .
(45)1036	0.5	50	.1035	— .0001
(46)1035	0.5	50	.1034	— .0001
(47)1012	0.5	50	.1011	— .0001

COPPER FROM CHROMIUM.

Chromium is not precipitated with the copper in a nitric (Luckow), sulphuric, or phosphoric acid (Smith) solution. A complete separation may also be made in a solution of the double oxalates (Classen).

In the following experiments, chromium equal to 100 per cent. of the copper was added in the form of chrome alum. In Nos. 51, 52 and 53 half the amount of copper was used, making the solution twice as dilute as in the first three, while the amount of chromium added was, by mistake, the same as used in the first three, making it equal to 200 per cent. of the copper.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(48)1040	0.5	50	.1040	. . .
(49)1047	0.5	50	.1048	+.0001
(50)1053	0.5	50	.1049	— .0004
(51)0498	0.3	50	.0500	+.0002
(52)0504	0.3	50	.0504	. . .
(53)0522	0.3	50	.0521	— .0001

COPPER FROM COBALT.

This separation can be made in a nitric (Luckow), sulphuric,

and phosphoric acid solution (Smith); also in a solution of the double oxalates (Classen).

Experiments, with cobalt equal to 100 per cent. of the copper, gave the following results:

No.	Copper Used. Gm.	Free H_2SO_4 . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(54)0502	0.3	50	.0502	. . .
(55)0444	0.3	50	.0442	—,0002
(56)1040	0.5	60	.1039	—,0001
(57)1046	0.5	60	.1046	. . .
(58)1034	1	50	.1034	. . .

COPPER FROM GOLD.

A solution of gold chloride was added to a solution of copper sulphate, and the mixture was evaporated with sulphuric acid until all the hydrochloric acid was driven off. This gave a solution of gold sulphate,* which, when diluted, decomposed with a partial separation of metallic gold. The filtrate was submitted to electrolysis. Since gold is easily deposited by the current (Luckow), that remaining in solution was precipitated with the copper. The metals were weighed together. The copper was then dissolved in dilute nitric acid, and the gold, after being carefully washed with water and alcohol, was dried and weighed. The difference in weight represented the amount of copper precipitated. Great care must be observed in washing the gold, since it adheres very loosely to the dish, and there is danger of mechanical loss. The first four results illustrate this point. The last two show that it possible to effect a good separation by this method. The original amount of gold present equaled 10 per cent. of the copper.

No.	Copper Used. Gm.	Free H_2SO_4 . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(59)0719	0.5	50	.0722	+ .0003
(60)0698	0.5	50	.0701	+ .0003
(61)0720	0.5	50	.0724	+ .0004
(62)0654	0.5	50	.0658	+ .0004
(63)0720	0.5	50	.0719	—,0001
(64)0654	0.5	50	.0653	—,0001

*Gmelin-Kraut's Handbuch der Chemie 3, 1014.

COPPER FROM IRON.

The presence of ferrous salts prevent the complete precipitation of copper (Boisbaudran). A quantitative separation can be made in nitric (Luckow), sulphuric (Luckow), and phosphoric acid (Smith) solutions, and in a solution of the double oxalates (Classen).

In ordinary cases the iron would be oxidized to the ferric state by the nitric acid used in effecting a solution, and in the following experiments ferric sulphate was added equal to 200 per cent. of the copper.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(65)0829	0.5	50	.0830	+.0001
(66)0917	0.5	50	.0917	. . .
(67)1173	. .	50	.1173	. . .
(68)1173	. .	50	.1172	— .0001

COPPER FROM LEAD.

In a nitric acid solution the lead separates completely as peroxide on the positive pole (Luckow). In a sulphuric acid solution it is completely removed as an insoluble salt. The separation cannot be made from a solution of the double oxalates (Classen).

Lead equal to 100 per cent. of the copper was converted into the sulphate and washed thoroughly with hot water.

The filtrates containing the copper gave the following results :

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(69)0502	0.3	40	.0502	. . .
(70)0520	0.3	40	.0519	— .0001
(71)1034	0.5	50	.1036	+.0002
(72)1045	0.5	50	.1041	— .0004
(73)1049	0.5	50	.1048	— .0001

COPPER FROM MAGNESIUM.

These metals may be separated in nitric and sulphuric acid so-

lution (Luckow); and in a solution of the double oxalates (Classen).

Magnesium equal to 10 per cent. of the copper was added to the solution in the form of sulphate. The following results were obtained:

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(74)1367	0.5	50	.1367	. . .
(75)1016	0.5	50	.1016	. . .
(76)1367	0.5	50	.1367	. . .
(77)1016	0.5	50	.1014	— .0002

COPPER FROM MANGANESE.

In nitric acid solutions the manganese separates completely as peroxide on the positive pole (Luckow). The separation of these metals can also be made in a sulphuric acid solution (Luckow), and in a solution of the double oxalates (Classen.)

During the electrolysis of an acid solution, some of the manganese is oxidized to permanganic acid, which may be recognized by a violet color at the positive pole. This has an injurious effect upon the precipitation of the copper (Luckow), which is shown below.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(78)1040	0.5	50	.1038	— .0002
(79)1038	0.5	50	.1034	— .0004
(80)0498	0.3	40	.0402	— .0096

The filtrates contained copper. The same thing was observed by the writer some years ago while working on a copper ore containing manganese. At that time a few cc. of alcohol were added to the solution to reduce the permanganate, and then the copper was easily precipitated.

In the following experiments enough alcohol was added to each assay to destroy the violet color. Manganese was added in the form of sulphate equal to 10 per cent. of the copper. Dishes were used for the negative electrodes, and there was considerable danger of the peroxide dropping from the positive pole.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(81)1047	0.5	50	.1047	. . .
(82)1049	0.5	50	.1054	+.0005
(83)1047	0.5	50	.1045	-.0002
(84)1049	0.5	50	.1050	+.0001
(85)0504	0.3	40	.0502	-.0002
(86)0521	0.3	40	.0520	-.0001

With manganese equal to 100 per cent. of the copper, and the alcohol added before starting the current, these results were obtained :

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(87)0502	0.3	40	.0502	. . .
(88)0442	0.3	40*	.0442	. . .

COPPER FROM MERCURY.

Copper cannot be separated from mercury by electrolysis in a nitric (Luckow) or sulphuric acid solution. Recent experiments have shown that the separation can be made from a solution in potassium cyanide when the copper does not exceed 20 per cent. of the mercury (Smith & Frankel).

In an acid solution mercury is deposited before the copper. It must therefore be removed as mercurous chloride by means of hydrochloric acid and a reducing agent, or by precipitating as a sulphide in a potassium cyanide solution.* Ammonium bisulphite proved unsatisfactory as a reducing agent, since it interfered with the subsequent precipitation of mercury by hydrochloric acid. Several experiments were made, but only a few were finished. In those recorded below, mercury was found deposited with the copper.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(89)0436	0.5-1	50	.0467	+.0031
(90)0423	0.5-1	50	.0453	+.0030

The other methods of separation were not tried.

*Fresenius' Quant. Anal.

COPPER FROM NICKEL.

A complete separation of these metals can be made in a nitric (Luckow), sulphuric (Gibbs, Boisbaudran, Luckow, Torrey & Eaton), or phosphoric acid (Smith) solution; also in a solution of the double oxalates. The following experiments were made with nickel equal to 10 per cent. of the copper present:

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(91)0393	0.3	40	.0399	+.0003
(92)0502	0.3	40	.0503	+.0001
(93)0444	0.3	40	.0444	. . .
(94)1034	0.5	50	.1034	. . .
(95)1041	0.5	50	.1040	-.0001
(96)1048	0.5	50	.1046	-.0002

The following assays contained nickel equal to 100 per cent. of the copper:

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(97)0826	0.5	50	.0826	. . .
(98)0826	0.5	50	.0825	-.0001
(99)0502	0.3	40	.0498	-.0004
(100)0442	0.3	40	.0438	-.0004
(101)0498	0.3	40	.0500	+.0002
(102)0438	0.3	40	.0441	+.0003

COPPER FROM POTASSIUM.

This separation is easily made in any of the solutions that have been mentioned. From a solution of the sulphate containing potassium equal to 10 per cent. of the copper, the following results were obtained:

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(103)1024	1	50	.1025	+.0001
(104)1029	1	50	.1029	. . .
(105)0680	0.5	50	.0680	. . .
(106)0709	0.5	50	.0709	. . .

COPPER FROM SILVER.

Copper cannot be separated from silver in nitric or sulphuric acid solutions (Luckow, Stillman, Torrey & Eaton, Stahl). Satisfactory results have been obtained from a solution in potassium cyanide (Smith & Frankel).

Preliminary separations may be made by reduction with tartaric acid (Luckow), by precipitation with hydrochloric acid, and by precipitation with ammonium oxalate (Classen).

Silver, when present in quantities as low as 1 to 3 per cent. of the copper, is deposited with the latter (Torrey & Eaton). This was confirmed by the following experiments. The filtrate contained no copper or silver, while the precipitated copper gave a test for silver.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(107)0829	0.5	50	.0848	+.0019
(108)0823	0.5	50	.0842	+.0019
(109)0917	1	50	.0942	+.0025

With the silver separated as chloride, the results were as follows :

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(110)0829	0.5	50	.0832	+.0003
(111)0823	0.5	50	.0825	+.0002
(112)0917	0.5	50	.0918	+.0001

Nos. 110 and 111 contained silver, which must have passed through the filter. The filtrates from the electrolysis contained no copper.

COPPER FROM SODIUM.

The electrolysis of the sulphates gave the following results :

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(113)1012	0.5	50	.1012	. . .
(114)1018	0.5	50	.1016	— .0002
(115)0674	0.5	50	.0674	. . .
(116)0703	0.5	50	.0703	. . .

COPPER FROM TIN.

Tin must first be separated from the copper by sodium sulphide, or as metastannic acid from a nitric or sulphuric acid solution.

Copper and tin were dissolved in nitric acid and evaporated with sulphuric acid. On diluting with 50 cc. water, the oxide of tin separated out and was filtered off. These precipitates in the first three assays were not washed thoroughly, and gave low results.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(117)0825	0.5	50	.0820	— .0005
(118)0814	0.5	50	.0807	— .0007
(119)0727	0.5	50	.0722	— .0005

The next series of assays contained more free acid, were diluted to 100 cc., and washed thoroughly with hot water.

No.	Copper Used. Gm.	Free H ₂ SO ₄ . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(120)0820	1	50	.0821	+ .0001
(121)0807	1	50	.0810	+ .0003
(122)0722	1	50	.0723	+ .0001

The filtrates from electrolysis gave no test for copper or tin. With sulphuric acid in excess the copper seems to be completely removed from the stannic oxide.

COPPER FROM ZINC.

These metals can be separated in nitric (Luckow), sulphuric (Boisbaudran, Torrey & Eaton), and phosphoric acid solutions (Smith); also, in a solution of the double oxalates. If a strong current is used with a nitric acid solution, the zinc is deposited on the copper as a black coating (Mackintosh).

In the following experiments zinc was added to equal 100 per cent. of the copper in each assay.

No.	Copper Used. Gm.	Free H_2SO_4 . cc.	Total Solution. cc.	Copper Found. Gm.	Difference in Weight. Gm.
(123)1368	0.5	50	.1366	— .0002
(124)1269	0.5	50	.1269	. . .
(125)1011	0.5	50	.1011	. . .
(126)1366	0.5	50	.1366	. . .
(127)1148	0.5	50	.1147	— .0001

It will be noticed in the experiments just described, and in the records of previous work, that the presence of certain metals produce inaccurate results in any solution when a simple electrolytic determination is made; and that these metals must be removed before the copper can be precipitated in a pure condition. This, however, can be done in nearly every case without serious difficulty.

GENERAL METHOD FOR ALLOYS.

Solution of the Alloy when Arsenic, Antimony (except in small quantities), Bismuth, Mercury, and Silver are Absent.—Dissolve from 0.2 to 0.5 gm. of the alloy (the amount of copper should not exceed 0.15 to 0.2 gm.) in a few cc. nitric acid, and add 10 drops concentrated sulphuric acid for each 0.1 gm. of the alloy taken. (If cadmium or tin is present, enough acid should be added to leave an excess of 1 cc. H_2SO_4 for each 0.1 gm. of that metal.) Evaporate until the heavy white fumes of SO_3 are driven off, allow to cool, dilute, and filter if necessary. The residue may be lead sulphate, metallic gold, or stannic acid. In the latter case the solution should be diluted to 100 cc., and heated for ten or fifteen minutes before filtering. Wash *thoroughly* with water, and evaporate the filtrate so that the solution for electrolysis will amount to 50 or 75 cc. If manganese is present, add 2 or 3 cc. alcohol to the solution before connecting with the battery.

Solution of the Alloy when the above Metals are Present.—Dissolve in nitric acid as before, and evaporate with hydrochloric acid to convert the metals into chlorides. Expel most of the free acid, dilute with water, and precipitate the metals with sulphuretted hydrogen. Separate the arsenic, antimony, tin and mercury by means of sodium sulphide.* Dissolve the remaining sulphides in nitric acid, and separate the copper by means of potassium cya-

*Fresenius Quant. Analysis.

nide, as directed by Fresenius.* Precipitate the copper from the final solution of the sulphate, as described below.

If only one of the above metals is present, separate the copper as directed under the separation of copper from other metals, or by some other reliable method.

Precipitation of the Copper.—The negative electrode, whether a dish or a cylinder of platinum, should be perfectly clean and as free as possible from dents and scratches. It should be allowed to remain in the balance case, before weighing, for five or ten minutes, until its weight is constant. The solution, when dishes are used, should not come higher than a quarter of an inch below the edge of the dish; this will leave sufficient surface to test for the end of the precipitation.

The positive electrode is best made from a No. 30 platinum wire with one end bent into a circle or spiral at right angles with the straight portion. Illustrations of these electrodes may be found in the text books, or in catalogues of chemical apparatus.

For solutions of the above strength the current should not exceed 0.3 to 0.4 cc. OH gas per minute, which is obtained when two gravity cells, having a capacity of one gallon each, are attached to one assay. A stronger current than this will deposit the copper in a spongy condition, and thus introduce sources of error. With more dilute solutions, however, a stronger current may be safely used, provided there are no other metals in solution that will be deposited by an increased current.

The time required for precipitating 0.1 gm. of copper was not determined, but, as stated before, the assays started late in the afternoon were usually finished the next morning, provided the ordinary temperature of the room was preserved.

The end of the precipitation is accurately determined by adding water to the solution, thus exposing a clean surface of the electrode. If no copper is deposited at the end of an hour, the precipitation is complete.

Washing the Copper.—This should be done with the current running, especially if much free acid is present. With dishes as electrodes, it may be done by means of a siphon, as described in the text books, water, of course, being supplied as fast as the so-

*Quant. Analysis.

lution is drawn out. With cylinders as electrodes it is more convenient to use the apparatus described by Glenn.* *In all cases cold water should be used.* After washing several times with water, the electrode is removed from the circuit, and washed once or twice with water, and finally with alcohol. The adhering alcohol, which should furnish just enough heat to dry the electrode without oxidizing the copper, is set on fire with a Bunsen burner and allowed to burn off.

The electrode should then be placed in a desiccator and allowed to cool, after which it may be weighed with the precautions mentioned above.

The determination of copper in brass and in German silver gave the following results :

No.	Brass Used. Gm.	Copper Found. Gm.	Difference in Weight of Copper Found. Gm.	Per cent. Copper.
(128)0974	.0662 }	.00009	67.964
(129)1914	.1300 }		67.892
(130)2068	.1404 }	.00006	67.920

No.	German Silver Used. Gm.	Copper Found. Gm.	Difference in Weight of Copper Found. Gm.	Per cent. Copper.
(131)1598	.0937 }	.0001	58.635
(132)1598	.0938 }		58.700

Still more closely agreeing results could have been obtained, no doubt, had larger samples been used.

GENERAL METHOD FOR ORES.

The method for dissolving ores has been described in detail by Glenn,† and need not be repeated here. Arsenic, antimony, bismuth, mercury, and silver, must be removed before submitting the solution to electrolysis. The remainder of the operation has been described under alloys. The method used by the Mansfield Copper Works is described as follows by Prof. Egleston in a recent number of the *School of Mines Quarterly*, (Vol. XII, 91).

"Two grams of the finely pulverized ore is placed in a porcelain crucible and heated in a muffle to drive off the volatile mat-

*Trans. A. I. M. E., Feb., 1889; this Journal 3, 344.

†Trans. A. I. M. E., Feb., 1889; this Journal 3, 342.

ter. It is then put into a beaker holding about 100 cc., and 10 cc. of a mixture of equal parts of nitric and sulphuric acid, with a few drops of muriatic acid poured on it, and heated on a sand bath to dryness. The dry material is taken up with a mixture of one part of nitric acid and six parts of water, and warmed. The beaker is filled to two-thirds of its height; a few drops of concentrated acetic acid is added to it and it is left for a short time. The whole is then submitted to an electrical current without filtration. The electrodes are a small cylinder of sheet platinum which is connected with the negative pole of a Meidinger battery, and a platinum spiral which is connected with the positive pole. The copper is deposited in eight or ten hours, and has a beautiful rose red color." This method is applied to the ores mined in the above district. "The ores are composed mostly of chalcopyrite and chalcosite, with small quantities of galena, blend, arsenopyrite and pyrite, associated with very small quantities of the ores of nickel and cobalt, and occur as slates in beds in the Permian formation between walls of sandstone and compact limestone." They contain from 2 to 10 per cent. copper and 0.01 to 0.04 per cent. silver.

Analysis of an oxidized ore in this laboratory gave the following results :

No.	Ore Used. Gm.	Copper Found. Gm.	Difference in Weight of Copper Found Gm.	Per cent. Copper.
(133)6190	.0151	.00003	2.440
(134)5975	.0146		2.443

Judging from the work of other chemists, and from the work done in this laboratory, I think we may safely conclude—

1st, That of all the solutions that have been used for the electrolysis of copper, the acid solution of the sulphate is the most accurate and the best adapted for general work ;

2d, That from no solution, so far as known, can copper be completely separated from all the metals with which it is associated by electrolysis alone ; and,

3rd, That in the absence of silver, mercury, bismuth, antimony, and arsenic, the method, as described, is one of the most accurate in chemical analysis.

THE ELECTROLYTIC METHOD APPLIED TO RHODIUM.*

BY EDGAR F. SMITH.

So far as I have been able to learn, the salts of rhodium have never been subjected to the action of the electric current. I, therefore, made experiments in this direction and obtained results indicating the possibility of employing the electrolytic method in the estimation of this metal. The various texts consulted led me to believe that in all likelihood a solution of the double cyanide of rhodium and an alkali metal would best answer my purposes. Precipitation did not occur upon mixing solutions of potassium cyanide and rhodio-sodium chloride. The liquid remained clear. As soon, however, as a comparatively feeble current acted upon the double cyanide, a reddish yellow colored compound appeared, and remained suspended in the liquid. It was probably a cyanide which sustained no change. I did not attempt a repetition of this experiment.

From my experience in the electrolysis of gold, platinum and palladium solutions containing alkaline phosphates and free phosphoric acid, I concluded to try rhodium under similar conditions. Sodium rhodium chloride, $\text{Na}_3\text{Rh}_2\text{Cl}_6 \cdot \text{H}_2\text{O}$, was the salt used by me. A sufficient quantity of it was dissolved so that 10 cc. of liquid contained, by calculation, 0.0980 gram of metallic rhodium.

Experiments.—No. 1. To 10 cc. of the rhodium solution were added 30 cc. of sodium phosphate, Na_2HPO_4 (sp. gr. 1.0358), and 3 cc. of phosphoric acid (sp. gr. 1.347). The total dilution of the electrolyte was 180 cc. The current gave 1.8 cc. OH gas per minute. In seven hours the deposition of metal was finished.

$$\begin{array}{rcll} \text{Weight of crucible + rhodium} & = & 63.4765 \\ \text{" " " " } & - & \text{" " } & = 63.3783 \\ \hline \text{Rhodium} & = & 0.0982 \end{array}$$

The deposition of metal occurred at the ordinary temperature. At the beginning of the decomposition the liquid showed a beautiful deep purple color, but as the metal separated, it rapidly be-

*Read before the Franklin Institute, Feb. 17, 1891.

came lighter and finally colorless. Upon inclining the dish in which the precipitation was made, thus exposing a fresh metal surface, the latter remained perfectly clear. The precipitation of metal was completed.

No. 2. The conditions here were nearly the same as in the preceding trial. The total dilution of liquid equaled 200 cc. while the current gave 1.6 cc. of OH gas per minute.

The metallic rhodium was precipitated upon copper-plated platinum dishes. It was rather black in color, very compact and perfectly adherent. It was washed without any difficulty. Hot water was used for this purpose. The drying was done upon a warm iron plate.

The results obtained accord so well with the theory that the accuracy of the method cannot be questioned. The rapidity with which the metal is deposited, and the ease with which it may be handled also recommend this method of estimation.

THE ELECTROLYTIC DETERMINATION OF MERCURY.*

BY EDGAR F. SMITH.

In gravimetric analysis mercury is frequently obtained as sulphide. To weigh it as such, or to convert it into some form suitable for weighing, requires much time and close attention to insure results that will be at all satisfactory. It is, therefore, better to have recourse to the electrolytic method of determination. As mercury sulphide dissolves quite readily in the fixed alkaline sulphides, I electrolyzed such solutions. The results show that this procedure affords a very accurate and clean method for the estimation of this metal.

The sodium sulphide was prepared as described in the paper relating to the determination of gold. Its specific gravity is 1.19.

Solutions of mercuric chloride, containing a known amount of metal, were first tried. The table shows the conditions of experiment and the results:

*Read before the Franklin Institute, Feb. 17, 1891.

Mercury Present in Grams.	Sodium Sulphide Present. Sp. gr. 1.29.	Total Dilution.	Current in cc. OH Gas per Minute.	Mercury Found.
0.1903	20 cc.	125 cc.	1 cc.	0.1902
0.1903	20 cc.	125 cc.	1 cc.	0.1905
0.1903	20 cc.	125 cc.	1 cc.	0.1907
0.1903	20 cc.	130 cc.	1.2 cc.	0.1910
0.1903	30 cc.	130 cc.	1.2 cc.	0.1900

The precipitation extended through the night. The deposited mercury was gray in color and very compact. Only once was a tendency to the fluid form observed. Hot water was used for washing. The metal was dried by holding the platinum dish in the palm of the hand and blowing gently upon the deposit.

If mercury and arsenic are both present in a solution of sodium sulphide, the current will throw out the former. It will not carry down any arsenic. This is evident from the two analyses that follow :

Mercury Present.	Arsenic Present.	Sodium Sulphide.	Total Dilution.	Current in cc. OH Gas per Minute.	Mercury Found.
0.1903 gr.	100 %	25 cc.	125 cc.	2 cc.	0.1908 gr.
0.1903 gr.	100 %	25 cc.	125 cc.	2 cc.	0.1894 gr.

In the communication upon the deposition of gold from sodium sulphide solutions, mention is made that gold and tin could not be separated electrolytically when present together in a solution of that kind. I was, therefore, rather surprised to discover that mercury could be separated from tin under such circumstances. The conditions of experiment were similar to the following :

The solution contained 0.1903 gram of mercury, 0.1200 tin, and 30 cc. of sodium sulphide. The total dilution was 125 cc. The current gave 2 cc. of OH gas per minute, and acted for twelve hours. The precipitated mercury weighed 0.1909 gram.

The filtrates from the mercury deposits did not show even traces of this metal when they were examined for the same.

THE ELECTROLYTIC DETERMINATION OF GOLD.*

BY EDGAR F. SMITH.

Gold has been estimated electrolytically in solutions, containing it as a double cyanide, or in the presence of sodium phosphate and phosphoric acid. From recent experiments I am satisfied it can be determined in the same manner by the decomposition of solutions of sodium sulphurate.

Years ago Parodi and Mascazzini (*Zeit. f. analyt. Chemie*, 18, 588) showed that antimony was completely precipitated from solutions of its ammonium sulpho-salt by the electric current. Classen elaborated this idea (*Ber.* 14, 1622; 17, 2467; 17, 2245; 18, 1110), substituting sodium sulphide for ammonium sulphide, and succeeded in effecting a most excellent separation of antimony from both tin and arsenic.

The sodium sulphide, used in the experiments recorded in this communication, was prepared by supersaturating a definite volume of caustic soda (1.3 sp. gr.) with hydrogen sulphide gas. An equal amount of caustic soda was then added, and the current of hydrogen sulphide continued for some hours through the solution. The liquid was then rapidly concentrated, until a crystalline scum appeared upon its surface. In this condition it was placed in bottles provided with tight-fitting corks. Crystals separated as the liquid cooled. These were recrystallized, and then dissolved for use. The specific gravity of their solution equaled 1.1800.

Experiments.—(1.) To a chloride solution of gold containing 0.1446 gram of metallic gold, were added 10 cc. of sodium sulphide (Na_2S), and 100 cc. of water. The electric current, allowed to act upon this mixture, gave 2.6 cc. OH gas per minute. The time of precipitation extended through the night.

The deposit of metallic gold weighed 0.1446 gram. It was bright yellow in color, and very adherent. Water alone was used to wash it. The drying was done upon a warm iron plate.

(2.) In this experiment the same quantity of gold was present as in the first trial. The volume of sodium sulphide did not exceed 20 cc., while the total dilution of the electrolyte was 100 cc. The current gave 2.6 cc. OH gas per minute. The metallic de-

*Read before the Franklin Institute, Feb. 17, 1891

posit was bright in appearance, firm and adherent. It weighed 0.1446 gram. The precipitation was complete in five and one-half hours.

The depositions of metal were made directly upon platinum. The gold was removed by covering it with a dilute solution of potassium cyanide, allowing the latter to remain for several hours in the dishes. When desired, the gold deposit can be very speedily removed by connecting the dish with the anode of a battery, and employing a platinum rod, which dips into the solution, as cathode. Platinum will not dissolve if feeble currents are used.

The results, given above, leave no doubt as to the applicability of this method in the estimation of gold.

Subsequent efforts were directed to its separation from other metals. As antimony can be deposited from a sodium sulphide solution by a current giving 1.5–2.0 cc. of OH gas per minute, I made no attempt to separate it from gold. The separation of gold from tin was much desired. Numerous trials were made. The results, however, were unsatisfactory. The gold was, in all instances, precipitated, but it carried down with it from one to three per cent. of tin. The sodium sulphide, in these separations, showed a specific gravity of 1.21. An additional gram of sodium hydroxide was introduced into the electrolyte for every centigram of metallic tin present. The current did not exceed 1.5 cc. of OH gas per minute. The dilution with water was 100 cc. While these conditions were exactly analogous to those in which antimony is separated from tin, they failed in the case of gold and tin.

Gold from Arsenic.—(1). The solution electrolyzed contained 0.1446 gram of gold, as chloride, 20 cc. of sodium arsenate solution (= 0.15920 gr. metallic arsenic), 60 cc. sodium sulphide, and 100 cc. of water. The current gave 1.2 cc. OH gas per minute. It ran through the night. The washed and dried deposit of gold weighed 0.1443 gram.

(2). With conditions similar to those in (1) the gold weighed 0.1446 gram.

Gold from Molybdenum.—(1). 0.1437 gram of gold, as chloride, 0.1500 gram molybdenum, as ammonium molybdate, 40 cc. of sodium sulphide, and 120 cc. water were exposed to the influence

of a current giving 0.7 cc. OH gas per minute. The time of deposition was twelve hours. The gold weighed 0.1430 gram.

(2). 0.1178 gram of gold, as chloride, 0.1200 gr. of molybdenum, 30 cc. of sodium sulphide (sp. gr. 1.12), and 100 cc. of water were electrolyzed with a current giving 2 cc. OH gas per minute.

The precipitated gold weighed 0.1172 gram. The current acted ten hours.

Gold from Tungsten.—(1). 0.1437 gram of metallic gold, as chloride, 0.1500 gram of tungsten, as ammonium tungstate, 20 cc. sodium sulphide (sp. gr. 1.17), and 100 cc. of water, gave 0.1440 gram gold, when electrolyzed with a current generating 1 cc. of OH gas per minute. The precipitation required twelve hours.

(2). In this trial 0.1440 gram of gold was found. The conditions were analogous to those of (1).

The gold deposits in all the separations were bright and compact. The same manner of washing and drying was pursued as in the first determination of the metal.

Gold was never discovered in the liquid removed from the deposit.

Qualitative trials proved that the separation of gold from vanadium, under conditions similar to those already mentioned, was also possible.

CHEMICAL LABORATORY OF THE UNIV. OF PA.,
PHILADELPHIA, FEB. 13, 1891.

ANIMAL MARINE AND VEGETABLE OILS USED IN LUBRICATION—THEIR CHEMICAL REACTIONS AND THE METHODS OF DETECTION IN MIXTURES.

BY PROF. THOS. B. STILLMAN.

During the past few years marked advances have been made in the qualitative and quantitative chemical reactions of many of the animal and vegetable oils, so that identification in mixtures has become more positive; yet the production of new oils by the distillation of waste fats and greases has opened up an enterprise to the manufacturer and a field of further inquiry to the chemist.

Many of these products form good lubricants, either alone or mixed with varying proportions of mineral oil, and they give

that "body" requisite, when moderate temperatures in lubrication are produced, that mineral oils often fail to possess.

The consumption of fish oils, especially refined menhaden oil, for similar purposes, has also largely increased, and in the cheaper grade of lubricants so much sophistication is practiced that in many instances four different oils have been found in one sample.

This adulteration is even more serious from a commercial standpoint, when oils of the finest quality and grades are so admixed that samples of absolutely pure sperm, whale, lard and olive oils are very difficult to obtain. The admixture of lard oil and cotton seed oil in olive oil, of menhaden oil in whale oil, of whale oil in sperm oil, of tallow oil in lard oil and in neatsfoot oil, all of which is now carried on as adulterations, complicates the subject of the chemical analysis of lubricating oils. When the above are used in the lubricant, and where it is desirable that two or, at most, three tests should be sufficient to identify an oil, it will be found that oftentimes six or seven different reactions are requisite.

In deciding upon what chemical tests constitute the criterion with all, or at least the majority of the oils used, so that a critical comparison can be made of their individual tests, and then a resume for tests in occurring mixtures, I have included the following :

1st. Specific Gravity. 2d. Maumenè's Test. 3d. Massie's Test, and Heidenreich's reaction with H_2SO_4 . 4th. Saponification Equivalent. 5th. Congealing or solidifying point. 6th. Iodine Absorption. 7th. Viscosity.

Experience has shown that the above tests will, in most cases, indicate any single oil absolutely, and in mixtures generally used for lubricating purposes, the animal, marine and vegetable, mixed with the mineral. In special cases, where two seed oils or two animal oils of similar chemical reactions are used with a mineral oil, the total adulteration will be indicated, and then identification of the like oils left for special tests.

Specific Gravity.

This important test is a confirmative one when a single oil is under examination, and an indicator in certain admixtures with mineral oils. Any abnormal figure obtained, either too high or too low, from the standard required, is indicative of the use of certain oils.

For instance, a lubricating oil of specific gravity .897, gave, upon saponification and separation, 30 per cent. of animal oil, and 70 per cent. of mineral oil of specific gravity .889. If a comparison be made of the specific gravity of the original oil, and the mineral oil separated therefrom, and the percentage of the latter taken into account, it will be found that the specific gravity of the remaining oil should be .916, which would indicate lard oil or neats-foot oil as the animal oil added, and the requisite confirmative tests can then be made.

It is true in many cases, where the adulteration has been made with two or even three oils of about the same specific gravity, that this test gives no *direct* indication of the oils composing the mixture (for instance, lard oil, specific gravity .916, olive oil, specific gravity, .917, and tallow oil, specific gravity, .915), yet the fact that the specific gravity is .916, and the oil entirely saponifiable, shows that a very considerable number of oils cannot be present in any quantity, such as rosin oil, cotton seed oil or menhaden oil, thus *indirectly* proving of value as an indicator.

Of the various methods and appliances used for the purpose of determining the specific gravity of lubricating oils, the author gives preference to the Westphal balance, as being expeditious and sufficiently accurate.

Where it is desirable to determine the gravities at higher temperatures than 20° C., the modification of the balance, as suggested by Bell (*Chem. Centrbl.*, 1879, 127), is used.

If small amounts of the oil only are obtainable, a small Picnometer, or the Araeo-picnometer of Eichhorn can be used. This invention (Deutsches Reichs Patent, No. 49, 683) is described by Dr. H. Hensoldt, of the Petrographical Laboratory of Columbia College, New York, in the "Scientific American Supplement" of March 21, 1891, with a drawing. The new and important feature of this instrument consists in a small glass bulb (attached to the spindle), which is filled with the liquid whose gravity is to be taken. Thus, instead of floating the entire apparatus in the test fluid, only a very small quantity of the latter is required.

The glass bulb, when filled with the test fluid, is closed by means of an accurately fitting glass stopper, and the instrument is then placed in a glass cylinder filled with distilled water at 17.5° C.

The gravity is then at once shown on the divided scale in upper portions of the spindle.

This apparatus is quite simple, very accurate, and will undoubtedly be of great use.

The following table converts degrees of the various hydrometers into specific gravity. [Liquids lighter than water.]

$$\left. \begin{array}{l} \text{Baumé hydrometer,} \\ \text{at } 15^{\circ} \text{ C.,} \end{array} \right\} \frac{144.78}{144.78 + n} = \text{specific gravity.}$$

$$\left. \begin{array}{l} \text{Brix hydrometer,} \\ \text{Fischer " at } 15.6^{\circ} \text{ C.,} \end{array} \right\} \frac{400}{400 + n} = \text{specific gravity.}$$

$$\text{Gay-Lussac, } 4^{\circ} \text{ C., } \frac{100}{100 + n} = \text{specific gravity.}$$

$$\text{Beck, } 12.5^{\circ} \text{ C., } \frac{170}{170 + n} = \text{specific gravity.}$$

$$\text{Cartier, } 12.5^{\circ} \text{ C., } \frac{136.8}{126.1 + n} = \text{specific gravity.}$$

n = degrees indicated upon the spindle.

For complete details regarding the apparatus used and methods employed in determining the specific gravity of fixed oils, consult:

"Untersuchungen der Fette, Oele and Wachsorten," by Dr. Carl Schaedler, pp. 38-40.

"Analyse der Fette and Wachsorten," by A. Benedikt, pp. 50-56.

"Commercial Organic Analysis," by A. H. Allen, pp. 13-18.

"Oils and Varnishes," by James Cameron, pp. 208-211.

"Spon's Encyclopedia of the Arts and Sciences," edited by C. G. W. Lock, p. 1465.

The following references include special methods relating to specific gravities and results obtained upon oils:

"The Adulteration of Fatty Oils," G. Richter, including specific gravities and the use of Laurot's Oleometer. *Seifenseid Zeitschrift*, vol. 16 p. 187, vol. 17 p. 199; also *Journal Society Chem. Industry*, Vol. 2, p. 384.

"Investigations on Lubricating Oils," S. Lamansky, *Ding. Poly. Journal*, 248, p. 29.

"The Methods of Examining and Chemistry of Fixed Oils," A. H. Allen. *Journal Society Chem. Industry*, Vol. 5., p. 65.

"On the Densities and Refractive Indices of Certain Oils," J. H. Long. Amer. Chem. Journal, Vol. 10, p. 392; also Journal Society Chem. Industry, Vol. 7.

"Specific Gravity of Some Fats and Oils," C. A. Crampton. Amer. Chem. Journal, Vol. 11, p. 232.

"Die Fette Oele," Dr. George Bornemann, pp. 231, 232.

"The Examination of Lubricating Oils," Thos. B. Stillman. The Stevens Indicator, Vol. 7, 1890, p. 211.

Maumenè's Test.

The rise of temperature produced when sulphuric acid is brought in contact with certain oils was first investigated by Maumenè, and the results of his experiments published in *Compt. Rend.*, Vol. 35, page 572.

The subject has been investigated by Fehling, Faist, L. Archbutt, C. J. Ellis, A. H. Allen and others, with the result that this test has been generally accepted as of importance in the distinction of many oils in mixtures.

Where a mixture of oils has been analyzed and the components recognized the proportions oftentimes can be determined by this reaction; that is to say, suppose the oil under examination to show a rise of temperature of 80°C., and the oils found by analysis to be lard oil and menhaden oil; their relative proportions can be determined by the following formulæ:

$$W_1 = W_3 \frac{t_3 - t_2}{t_1 - t_2}$$

$$W_2 = W_3 \frac{t_3 - t_1}{t_2 - t_1}$$

W_1 = proportion by weight of menhaden oil.

W_2 = " " " lard "

W_3 = weight of mixture.

t_1 = temperature of menhaden oil.

t_2 = " " lard "

t_3 = " " mixture

Lard oil alone when treated with sulphuric acid gives a rise of temperature of 40°C., menhaden oil, under similar conditions, a rise of 128°C. Using these values in the above formulæ we obtain 54.6 per cent. lard oil and 45.4 per cent. menhaden oil.

In a mixture containing a mineral oil mixed with an animal, marine or vegetable oil the distinction would be even more pronounced, since the mineral oil shows but a very slight increase of temperature (generally from 2°C. to 5°C). The increment of temperature would be dependent upon the other oil added to the mineral oil.

Briefly stated, the rise of temperature of the following oils would be :

	NAME OF OBSERVER.				
	Maumenè.	Schaedler.	Archbutt.	Allen.	Stillman.
	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.
Lard oil	40	41	39.5
Tallow oil	41-43	39
Neats-foot oil	45	50	43	. . .	40
Oleo oil	37½	38½	37
Elain oil	38
Sperm oil	51	45-47	48
Whale oil	92	91	92
Menhaden oil	123-128	126	128
Dog-fish oil	80
Cod liver oil	102-103	103	. . .	113	110
Crude cotton-seed oil	69.5	70	67-69	74
Refined " "	75-79	74-75	78
Rape oil	58 F.	60
Castor oil	47	48	46	65	45
Olive oil	42	43	41-45	41-43	42
Rosin oil	28	. . .	18-22	10
Mineral Lubricating oil	3-4	3
Earth-nut	67	67	47-60
Rosin oil, 1st run	33
" " 2d "	10
" " 3d "	10
Sea Elephant	65

It will be noticed that Schaedler gives a rise of temperature of 28° for Rosin oil ; Allen, a rise of 18° to 22° for the same oil, and that my determination was 10°.

A difference so great led me to obtain the various grades of Rosin oil, "1st, 2d and 3d runs," when the above discrepancy was easily explained.

Rosin oil of the "1st run" is a white, opaque, thick liquid, containing all of the water of the rosin from which it was distilled, and it is this water that causes the rise of temperature above 10° when the oil is mixed with the sulphuric acid.

Rosin oils of the "2d and 3d runs" are clear, limpid, dark-red colored fluids, practically free from water, and when treated with H_2SO_4 do not indicate more than 10° rise of temperature.

From these tests I conclude that both Schaedler and Allen tested rosin oil that was a mixture of the "1st and 2d runs," or of an oil not properly separated into the different distillates.

The method of applying this test will be found in *Untersuchungen der Fette, Oele und Wachsorten*," Dr. Carl Schaedler, pp. 120-123.

"Analyse der Fette und Wachsorten," Dr. R. Benedikt, pp. 190-191.

"Spon's Encyclopedia," p. 1471, gives a modification of the process in which sulphuric acid of 1.845 is used. Consult also,

"Chemical News," Vol. 43, p. 195.

Archbutt, "Journal Society Chem. Industry," Vol. 5, p. 303.

C. J. Ellis, "Journal Society Chem. Industry," Vol. 5, p. 150.

A. H. Allen, "The Analyst," Vol. 2, p. 102.

Maumenè, "The Chemical News," Vol. 40, p. 46.

Stillman, "Journal Analytical Chemistry," Vol. 3, p. 366.

Casselmann, "Ztschr. für anal. Chem.," Vol. 6, p. 484.

Maumenè, "Compt. Rend., 92, p. 721.

Dr. G. Bornemann, "Die Fetten Oele," p. 228.

Color Reactions of Oils with Nitric and Sulphuric Acids.

Of the many color tests introduced for the identification of simple oils, preference is given to Heidenreich's sulphuric acid test and Massie's nitric acid test.

The color reactions of Chateau* in which barium polysulphide, zinc chloride, stannic chloride, phosphoric acid and mercuric nitrate, in solutions, are used, while very interesting, seldom are of any advantage over the two tests noted above. Glassner's† nitric acid reactions are practically the same in results as Massie's, so that no advantage would be obtained in including the former.

Heidenreich's test is as follows :

A clear glass plate is placed over a piece of white paper, ten drops of the oil under examination are placed thereon, and one drop of concentrated sulphuric is added.

The color produced when the acid comes in contact with the

*Spon's Encyclopedia, Vol. IV., pp. 1472-1475.

†Chem. Centr., 1873, p. 57.

oil is noticed as well as the color produced when the two are stirred with a glass rod. Many oils give off characteristic odors during the reaction, especially neats-foot oil, whale oil and menhaden oil.

Massie's Test is thus performed :

Nitric acid of specific gravity 1.40, free from nitrous acid is mixed in a test tube with one-third its volume of the oil, and the whole agitated for two minutes.

The color of the oil after separation from the acid is the indication.

In mixtures of oils, the characteristic colors produced, by either Heidenreich's or Massie's tests, are often clouded, and in many instances no inferences can be drawn, yet with single oils the reactions are often distinctive and sufficiently strong to give confirmatory results.

In cod-liver oil, or whale oil, when mixed with a mineral or even vegetable oil, the characteristic brilliant violet color produced with sulphuric acid cannot be mistaken. This color, due to the presence of cholic acid, is found in most of the fish oils, but is much more pronounced in cod-liver oil.

The following table will indicate the colors produced by Heidenreich's and Massie's tests.

	HEIDENREICH'S TEST.		MASSIE'S TEST.
	Before Stirring.	After Stirring.	
Lard oil	Yellow	Brown	Yellow.
Tallow oil	Yellow	Orange	Colorless.
Neats-foot oil	Yellowish	Red brown	Red.
Oleo oil	Colorless	Orange	Pink.
Elain oil	Light green (turning to brown)	Brown	Orange red.
Sperm oil	Brown with purple streaks	Reddish brown	Red.
Whale oil	Red violet	Violet brown	Red.
Menhaden oil	Red	Brown	Dark red.
Dog-fish oil	Violet	Dark brown	Orange.
Cod-liver oil	Red violet	Dark brown	Orange red.
Crude cotton seed	Brilliant red	Brown	Brown.
Refined " "	Reddish brown	Red	Orange red.
Rape oil	Yellow brown	Brown	Orange.
Castor oil	Light yellow to brown	Pale brown	Orange.
Olive oil	Light green	Greenish to light brown	Yellow to greenish.
Rosin oil	Brown	Brown	Orange.
Earth-nut oil	Yellow to orange	Greenish	Reddish.

Full details regarding these tests will be found in :

"Oils and Varnishes," Cameron, p. 234.

"Dictionary of Chemistry," Watts, Vol. III., p. 1428.

and in connection with the use of sulphuric or nitric acid in the qualitative examination of oils by other chemists, the following references are given :

A. Andoyand, "Compt. Rend.," Vol. 101, p. 752.

Flückiger, "Ztschr. für anal. Chem.," Vol. 10, p. 235.

Allen, "Moniteur Scientif.," Vol. 14, p. 724.

H. Levy, "Chem. Zeit. Rep.," Vol. 12, p. 238.

A. Kremel, "Chem. Zeit. Rep.," Vol. 13, p. 46.

Stillman, "Jour. Anal. Chem.," Vol. 3, p. 368.

Pontat, "Chem. Ztg.;" also "Chem. News," Vol. 39, p. 136.

Wideman, "Moniteur Scientif. Ques.," May, 1881.

M. Zecchini, "Les Mondes," May 13, 1882.

H. Meyer, "Zeit. für anal. Chem.," Vol. 23, Part III.

J. L. Rossler, "Zeit. für anal. Chem.," Vol. 24, Part III.

R. Brulle, "The Chemical News," Vol. 57, p. 211.

Saponification Equivalent

The "saponification equivalent" of any oil is the number of gms. of the oil decomposed by one litre of a normal solution of an alkali.

The method, as given by Koettstorfer will be found in "Zeit. für anal. Chem.," Vol. 18., page 199.

More complete details of the process will be found, however, in Schaedler, "Untersuchungen der Fette, Oele," etc., pages 130-136.

The procedure is as follows :*

Two gms. of oil are weighed in a tall beaker (75 cc. capacity), 25 cc. standard alcoholic potash are added, and the whole heated on a water-bath. When saponification is complete, the solution is taken from the water-bath, 1 cc. of alcoholic phenolphthalein is added, and it is titrated back with half-normal hydrochloric acid.

From the difference between the amounts of hydrochloric acid required by 25 cc. standard alkali, and the amount used in the above titration, the amount of KHO, combined with the acids of fat is calculated. The standard potash solution is to be titrated

*Oils and Varnishes, Cameron, p. 247.

afresh on each occasion, and before testing with the standard acid, 25 cc. of it should be heated for fifteen minutes on a water-bath, as in the saponification of the sample.

	Saponification Equivalent.	Percentage of KHO for Saponification.
Lard oil	285—296	19.1 to 19.6
Tallow oil	285—296	19.1 to 19.6
Neats-foot oil	285—300	19.2 to 20.3
Sperm oil	380—454	12.34 to 14.74
Whale oil	250—303	18.85 to 22.44
Menhaden oil	250—303	19.2
Cod-liver oil	250—303	18.5 to 21.3
Crude cottonseed oil	285—296	19.10 to 19.66
Rape oil	313—330	17.02 to 17.64
Castor oil	309—319	17.60 to 18.15
Olive oil	285—296	19.1 to 19.6
Rosin oil	290—330	17. to 19.3
Earth-nut oil	285—296	19.13 to 19.66

The Cold Test.

The degree at which an oil becomes semi-solid and refuses to flow freely is considered the "Cold Test," and is performed as follows :

100 cc. of the oil are transferred to a narrow bottle (capacity 200 cc.), stoppered with a rubber stopper, through which is inserted a thermometer, the bulb of which reaches an inch or more into the oil.

The bottle is placed in a mixture of ice and salt, or other freezing compound, and retained there until the oil becomes solid. It is then removed and allowed to warm until the contents become somewhat thinner in consistence. The bottle is inclined from side to side until the oil *begins* to flow, when the temperature is taken.

At this particular temperature the oil is neither at its normal fluidity, nor is it solid, and while this method does not correctly indicate the exact temperature of the solidifying point, it does show the point at which the oil ceases to flow readily ; the important one to the oil inspector.

In lubricating oils, to be used in railroad practice, this "cold test" is a vital one, and receives in the laboratories of the different railroads of the United States considerable attention.

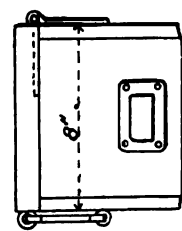
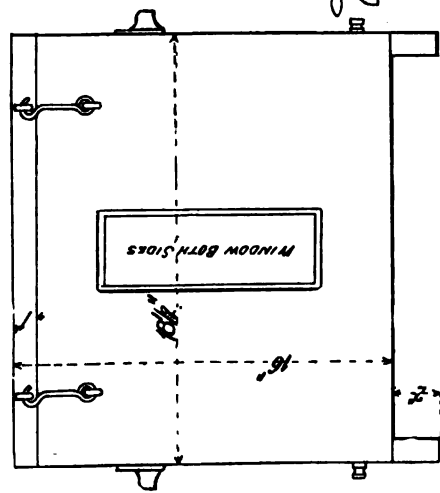
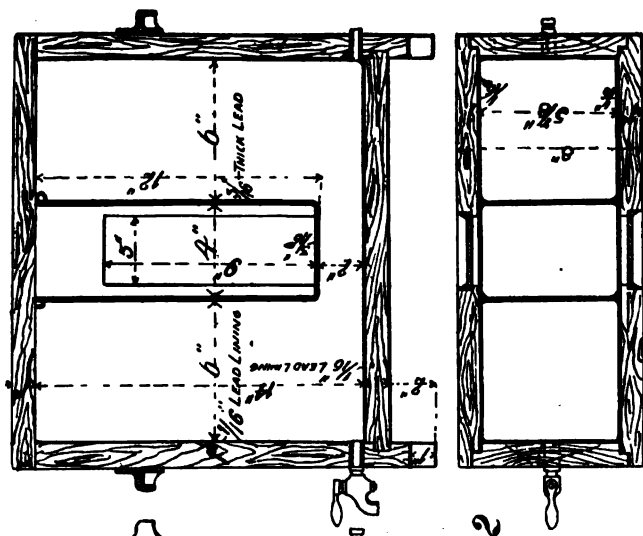
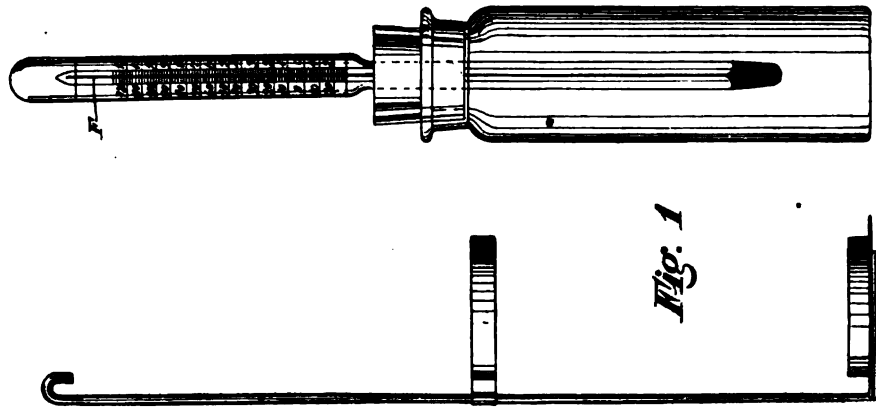


Fig. 2

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A mineral lubricating oil, "non-paraffine," of good quality, does not show any material difference in its consistency at 25° C. or 10° C., but a radical change would be indicated at 10° C. if some of the animal or vegetable oils were a component.

While it is true that no proportion of one or the other can be indicated by the "cold test," and that this test might not properly be classed as a chemical but rather as a physical one, yet so important is this property of congealing in lubrication, and as all laboratories connected with railroad work rely strongly upon it, I have included it as one of the principal ones.

In connection therewith is here included the drawings of the apparatus used for this purpose in the chemical laboratory of the Chicago, Burlington and Quincy R. R. Co., Aurora, Ill. (Geo. H. Ellis, Chief Chemist).

Figure 1 represents the glass apparatus with the thermometer arranged for the "cold test."

Figure 2 represents the "cold box" to contain the freezing mixture and in which the oil is tested.

In the specifications, for the supply of oils to the various railroads, it is generally stated what degree is required for the "cold test." Thus the P. R. R. requires as follows:

Lard oil, 8°C., November 1 to April 1.
Tallow oil, 8°C., " "
Neats-foot oil, 8°C., " "

B. & O. R. R. Co.:

Engine oil. — From October 1 to May 1, below 9°C.
Passenger car oil. — " " " "
Freight car oil. — " " " "

C., B. & Q. R. R. Co.—Black Engine oils:

"Summer oil" must flow at 15°C. and above.
"25°" oil " " — 1°C. "
"15°" oil " " — 9°C. "
"Zero" oil " " — 15°C. "

The following determinations of the "cold test" made in my laboratory will show the wide range between many of the oils in this regard used in lubrication:

Elaine oil	6 degrees C.	"Light strained"	
Saponified red oil	5 " "	menhaden oil	7 degrees C.
Prime neats-foot oil, —	4 " "	"Natural winter"	
White neats-foot oil, —	4 " "	menhaden oil	9 " "
Pure "hoof" oil	6 " "	"Bleached winter"	
Prime lard oil	7 " "	menhaden oil	12 " "
"No. 1" lard oil	7 " "	"Extra bleached winter"	
"XXX" lard oil	3 " "	white menhaden oil	11 " "
American sod oil	1 " "	"Bank" oil	4 " "
English "	24 " "	"Straits" oil	7 " "
Tallow oil	26 " "	Sea elephant oil	5 " "
Dog-fish oil	7 " "	"Black fish" oil	8 " "
"Right" whale (Pacific)	0 " "	Rosin oil, "1st run"	3 " "
Unbleached "bow-head" whale (Pacific)	7 " "	" " "2nd run"	19 " "
"Bleached" whale oil (Pacific)	13 " "	" " "3rd run"	20 " "
"Natural" sperm oil (Pacific)	0 " "	Castor oil	18 " "
Bleached sperm oil (Pacific)	4 " "	"Crude" cotton-seed oil	7 " "
Herring oil (Pacific)	0 " "	"Prime summer" yellow cottonseed oil	5 " "
"Natural winter" sperm oil (Atlantic)	1 " "	"Off quality" summer yellow cottonseed oil	6 " "
"Bleached winter" sperm oil (Atlantic)	4 " "	"Prime quality winter" yellow cottonseed oil	10 " "
"Natural spring" sperm oil (Atlantic)	10 " "	"Off quality" winter yellow cottonseed oil	8 " "
"Bleached spring" sperm oil (Atlantic)	8 " "	"Prime quality" summer white cottonseed oil	3 " "
"Natural winter" whale oil (Atlantic)	2 " "	"Off quality" summer white cottonseed oil	8 " "
"Bleached winter" whale oil (Atlantic)	5 " "	"Prime quality" winter white cottonseed oil	9 " "
"Natural spring" whale oil (Atlantic)	5 " "	"Off quality" winter white cottonseed oil	5 " "
"Bleached spring" whale oil (Atlantic)	2 " "	"No. 1" French "Degras" oil	25 " "
"Prime crude" menhaden oil	4 " "	"No. 2" French "Degras" oil	25 " "
"Brown strained" menhaden oil	7 " "	English "Degras" oil	18 " "
		Olive oil	3 " "
		"Oleo" oil	25 " "

[TO BE CONTINUED.]

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Chromium.—The atomic weight of this element has been re-determined by Meineke, who adopts several distinct methods.

1st. Normal silver chromate, Ag_2CrO_4 , was reduced by hydrochloric acid and alcohol. The silver chloride was filtered off, and weighed; a small trace which remained in solution being thrown down as sulphide and weighed as sulphate. In the filtrate the Cr_2O_3 was also estimated.

2nd. Silver ammonio-chromate, $\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3$ was similarly treated. In this and the preceding series of experiments, the atomic weight derived was computed from the ratio $4\text{Ag Cl} : \text{Cr}_2\text{O}_3$.

3rd. Iodometric experiments with silver chromate. Potassium iodide reduces dilute solutions of chromic acid, and the amount of reaction can be measured by titration with sodium thiosulphate. Thus the oxygen in excess of $\text{Ag}_2\text{O} + \text{Cr}_2\text{O}_3$ can be estimated.

4th. Similar iodometric tests with silver ammonio-chromate.

5th. Iodometric titrations with potassium dichromate. In this series and the next the acid iodate KHI_2O_6 was used instead of potassium iodide.

6th. Iodometric titrations with ammonium dichromate.

7th. Estimation of Cr_2O_3 in ammonium dichromate, by precipitation with mercurous nitrate and ignition of the precipitate.

The seven series gave values for Cr as follows: Series 1 and 3 were computed together, so also were series 2 and 4; that is, 3 serves as a correction to 1, and 4 to 2.

Series.	1.	2.	5.	6.	7.
Cr =	52.00	52.12	51.94	51.93	51.97
	51.92	52.00	51.95	51.94	51.96
	51.98	51.95	51.89	51.96	51.98
	51.98		51.90	51.91	52.00
	51.96		51.96	51.98	52.06
	52.04		51.83	51.93	
			51.95	51.94	
			51.94	51.92	
			51.85	51.93	
			51.95		
			51.94		
			51.88		
Mean,	51.98	52.02	51.91	51.94	51.99

Series 3 applied to series 1 gives Cr = 52.00.

Series 4 applied to series 2 gives Cr = 52.04.

The author regards the value 51.94 as the most probable. This

is with $O = 15.96$, $Cl = 35.37$, $Ag = 107.66$, etc. All weights were reduced to a vacuum.—*Ann. der Chem.*, **261**, 339.

Copper.—Richards, in continuation of his former work, now determines the atomic weight of copper from analyses of cupric bromide. The latter salt was not weighed directly, but in solution; and ratios were determined as follows, omitting certain "preliminary series" of experiments, which agree closely with the "final" data:

1st. In weighed quantities of $CuBr$, solution, the copper was determined electrolytically.

2nd. In weighed quantities of solution, the bromine was determined as silver bromide. From the weight of the latter, the Br was computed by means of the ratio $Ag : Br :: 108 : 80.007$.

3rd. In weighed quantities of solution, the bromine was precipitated by a solution containing a known weight of silver, the end reaction being ascertained volumetrically.

All the data, with reduction of weights to vacuum, and to equal quantities, viz., to 50 gms. of $CuBr$, solution, are as follows:

<i>In 50 Gms. Solution.</i>		
Cu.	Br.	Equiv. Ag.
0.54755	1.3767	1.8586
.54750	1.3762	1.8579
	1.3766	1.8583
Mean, 0.54753	1.3765	1.8583

Hence, when $Ag = 108$ (the standard of comparison), and $Br = 80.007$,

$Cu = 63.645$, mean of all.
 63.664 , highest value.
 63.628 , lowest value.

When $O = 16$ and $Ag = 107.93$, $Cu = 63.6$, a value closely agreeing with Richards' earlier determination.

Incidentally, as a check upon the work, Richards also determines the ratio between Ag and Br , which can also be computed from the data given above. The results, direct and indirect, for the percentage of Ag in $AgBr$ are as follows:

Direct.	Indirect.
57.447	57.454
57.455	57.448
57.446	57.447
Mean, 57.449	57.448

Stas. found 57.445.—*Proc. Amer. Acad.* **25**, 195.

Rhodium.—Seubert and Kobbé determine this atomic weight by reduction of the salt $\text{Rh}(\text{NH}_4)_2\text{Cl}_2$ in hydrogen. Weights as follows :

1.8585 gm. of salt	gave 0.6496 Rh, or		34.953 per cent.	
1.5560	"	"	.5435	" 34.929 "
1.5202	"	"	.5310	" 34.930 "
2.0111	"	"	.7031	" 34.961 "
1.8674	"	"	.6528	" 34.958 "
2.4347	"	"	.8513	" 34.965 "
2.3849	"	"	.8338	" 34.962 "
2.5393	"	"	.8881	" 34.974 "
1.4080	"	"	.4920	" 34.943 "
1.4654	"	"	.5123	" 34.960 "
Sum, 19.0455		Sum, 6.6575	Mean, 34.954	

Hence, if $\text{O} = 15.96$ and with the Meyer-Seubert values for N and Cl, $\text{Rh} = 102.728$, with maximum and minimum values 102.811 and 102.609. Reducing the weights to a vacuum basis, $\text{Rh} = 102.652$.

In the sixth experiment, the ammonium chloride given off was collected in a bulb tube and estimated as silver chloride. The weight of the latter was 3.5531 gms. Hence, $\text{Rh} = 102.864$, from the ratio of the whole salt to AgCl , and 102.804 from the ratio of Rh to AgCl . The final conclusion of the authors is, that 102.7 may be taken as the atomic weight in question. If $\text{O} = 16$, this becomes 102.96.—*Ann. d. Chem.*, **260**, 314.

Osmium.—Redetermined by Seubert, who studied the salts K_2OsCl_6 and $(\text{NH}_4)_2\text{OsCl}_6$. By reduction of the potassium salt in hydrogen and volatilization of the KCl ; the following data were obtained :

1.1863 gm. of salt	gave 0.4691 Os, or		39.543 per cent.	
.9279	"	"	.3667	" 39.519 "
1.0946	"	"	.4330	" 39.558 "
1.6055	"	"	.6351	" 39.558 "
.4495	"	"	.1778	" 39.555 "
.8646	"	"	.3417	" 39.521 "
.7024	"	"	.2781	" 39.593 "
1.2742	"	"	.5041	" 39.562 "
1.0466	"	"	.4141	" 39.566 "
Sum, 9.1516		Sum, 3.6197	Mean, 39.553	

2.2032 gm. of salt gave 0.6820 KCl, or 30.955 per cent.

2.0394	"	"	.6312	"	30.950
2.7596	"	"	.8544	"	30.961
2.4934	"	"	.7710	"	30.922
2.8606	"	"	.8843	"	30.913
1.8668	"	"	.5768	"	30.898
1.2227	"	"	.3778	"	30.899

Sum, 15.4457

Sum, 4.7775

Mean, 30.931

With the salt $(\text{NH}_4)_2\text{OsCl}_6$, two experiments were as follows :

2.6687 gms. salt gave 1.1597 Os, or 43.456 per cent.

2.6937	"	"	1.1706	"	43.457	"
--------	---	---	--------	---	--------	---

Sum, 5.3624

Sum, 2.3303

Mean, 43.4565

Taking the sums of the series with K_2OsCl_6 , and using the Meyer-Seubert atomic weights with $\text{O} = 15.96$, we have :

From $\text{K}_2\text{OsCl}_6 : \text{Os}$;	$\text{Os} = 189.92$.
" " : 2KCl ;	" = 190.80.
" $\text{Os} : 2\text{KCl}$;	" = 190.268.
" $(\text{NH}_4)_2\text{OsCl}_6 : \text{Os}$	" = 190.76.

Rejecting the last value, and taking a general mean of all the experiments upon the potassium salt, Seubert finds $\text{Os} = 190.33$, when $\text{O} = 15.96$. With $\text{O} = 16$, Os becomes 190.78.—*Ann. d. Chem.* 261, 258.

Miscellaneous.—Following the preceding paper, Seubert gives a general discussion of the atomic weights of the platinum group; and, including gold and silver, shows that they follow the order required by the periodic law.—*Ann. d. Chem.* 261, 272.

Schneider (*Jour. Prakt. Chem.* (2), 42, 553) criticises Classen's work on bismuth. In the same journal, (43, 133) Classen replies.

A recalculation of Partridges' determination of the atomic weights of cadmium, entitled, "On the question of concordance in determinations of atomic weights," has been published by Clarke.—*Am. Chem. Jour.* 13, 34.

LOSS OF CARBON IN RUSTED PIG IRON.

Weighed samples having stood in beakers until much rusted, were analyzed and gave the following results for total carbon :

	No. 1	No. 2
Rusted Drillings	1.941	1.332
Original Sample	2.282	2.132

The combined carbon in each of the samples was found to be as follows:

No. 1	0.378 per cent.
No. 2	0.336 per cent.

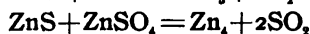
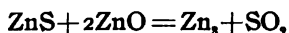
Showing that part of the graphite had disappeared as a result of the rusting. The greater loss in No. 2 is explained by the fact that the drillings were much finer in that case.—(J. G. Donald, Chem. News, 68, 73.)

A. H. W.

ON THE CURIOUS BEHAVIOR OF CERTAIN ZINC SULPHIDE COMPOUNDS.

The method of preparing zinc sulphide pigments is described as follows: Zinc sulphate or chloride free from iron, manganese, lead, tin, etc., is precipitated by an alkaline or alkaline-earth sulphide. The precipitate, which consists of hydrated zincsulphide alone, or admixed with a sulphate of an alkaline earth, is dried and ignited at a red heat, thrown while red hot into water, levigated, washed, dried again, and reduced to a fine powder, when the pigment is ready for grinding in oil as a paint. It is said that this product is superior as a pigment to the best white lead in respect to whiteness, body, and covering power. It is relatively harmless and is discolored by H_2S , but the chief difficulty is the fact that it darkens when exposed to sunlight, but the curious circumstance is mentioned that the darkened pigment, after being placed in the dark for a few hours, completely regains its whiteness and afterwards seems less sensitive to the light than before.

The dry hydrated zinc sulphide does not darken before ignition. Some of the whitest and purest zinc blende obtainable was experimented with and it was found that after calcining so as to slightly oxidize it, it darkened readily, though before calcination no change took place. Zinc sulphide, prepared by burning zinc in an atmosphere of sulphur vapor, and collecting the product in a chamber, the temperature of which was sufficiently high to prevent the condensation of sulphur, exhibited the same phenomenon. The color developed in the pigment by light bears a resemblance to that of the finally divided metal deposited from certain metallic solutions. When hydrated zinc sulphide is ignited, even when air is excluded, zinc is reduced according to the reactions:



and the author thought that light might be able under certain conditions to produce the changes which heat does. According to this theory the darkening was due to the formation of a film of metallic zinc, but later discovered facts proved this theory untenable. A sample dried at 120° C., and sealed, while warm, in a glass tube, showed no darkening even after one years exposure. A thorough drying of the pigment immediately before grinding in linseed oil, as a practical application of the above observation, was not found satisfactory. As sensitiveness to light was found to be enormously increased by moistening with a dilute solution of zinc sulphate, it was thought that perhaps the darkening might be due to imperfect washing but the most thorough washing failed to remove the basic zinc sulphate formed during ignition. Solutions of the hydrates of potassium, sodium, barium, and calcium were used to attempt to decompose this sulphate into oxide. The first three reagents were rejected as they seemed to attack the zinc sulphide itself, and lime-water, though for a time it seemed to exercise a protective effect, afterwards apparently lost its power of making the sulphide resistant to light. 0.5 per cent. of freshly precipitated magnesium hydrate, mixed with the zinc sulphide precipitate, gave the best results, but somewhat impaired its general qualities. The results of several years experience led to the adoption of the following method of manufacture: The zinc-salt and barium sulphide were concentrated as far as practicable, the sulphide being used at a boiling temperature, and the precipitate was readily filtered. 0.5 per cent. of freshly precipitated magnesium hydrate was added to the vat containing the precipitate, together with some finely powdered salt. After drying, the precipitate was crushed to the size of small beans and mixed with three per cent. ammonium chloride before ignition, but the explanation of the way in which the latter acts, is not known to the author. The use of salt was to prevent fritting; the salt, in the heat of the furnace, forming a glaze which protected the particles, while it readily dissolved when the mass was thrown into water. By this process, a pigment was made which stood the severest tests of exposure to light, except in the case of one or two batches,

which for some unknown reasons, were more or less sensitive. (John Cawley, Chem. News, 63, 88.)

A. H. W.

A METHOD FOR THE TITRATION OF COBALT.

It was found, while studying the Wolff method for manganese, that cobaltous oxide, in presence of zinc oxide, was oxidized by an excess of permanganate solution, and the following method was devised.

The neutral solution of cobalt is put into an Erlenmeyer flask, diluted to 300 cc., and 5-10 cc. of zinc oxide milk added. The liquid is then brought to the boiling point, and permanganate of potash solution added until there is an excess of from 5 cc. to 10 cc. The liquid is then boiled for about ten minutes, when 30 cc. of zinc chloride solution (made by satisfying oxide of zinc by dilute hydrochloric acid [1-19]), is added, and the liquid then titrated back with arsenious acid.

It is essential that the solution at the start be neutral or freed from acid by evaporation to dryness. If a sulphate, $\text{Ba}(\text{NO}_3)_2$, is added in excess. (M. A. Von Reis and F. Wiggert, Ztschr. angew. Chem., 1890, 695.)

J. E. W.

ON THE ESTIMATION OF NITRATES BY MEANS OF ALUMINUM.

Metallic aluminum obtained by the modern methods is considered by the author to be better for determining nitrogen than that produced by means of sodium. The traces of sodium left alloyed with the aluminum is the objectionable point.

For the determination, the author used 50 cc. of the nitrate solution (10 gms. KNO_3 ,—1 liter H_2O) in an Erlenmeyer flask, diluted to 150 cc., and added 20-25 cc. NaOH solution (32°Be). After being well mixed, 2 to 3 gms. of aluminum foil is put into the flask, and the tube of a condensing apparatus is attached. This is allowed to stand over night, and the following morning the ammonia is distilled.

On account of the formation of hydrogen, it is necessary that the exit end of the condenser be placed under H_2SO_4 , so as to prevent any unabsorbed ammonia from passing off with it. (A. Stutzer, Ztschr. angew. Chem., 1890, 695.)

J. E. W.

ESTIMATION OF OXYGEN IN GAS MIXTURES.

After considerable investigation, the following solution for the absorption of oxygen was decided upon :

A.—40 gms. crystals sulphate of iron.

B.—30 gms. Rochelle salts.

C.—60 gms. commercial caustic potash.

Each is dissolved in 100 cc. H_2O .

Pour one volume of *A* into five volumes of *B*. This gives a white precipitate, which, on the addition of one volume of *C*, disappears. It is to be noticed that if the solutions are not mixed as directed, a clear solution will not result. The solution, when ready for use, should be clear and of a yellowish color. This gradually turns to a greenish hue by the oxidation of the inflowing gas. Four experiments on air, using a Hempel pipette, gave the author a mean of 10.5 cc. in 50 cc. of gas, equivalent to 21.0 per cent. O. (L. L. de Koninck, *Ztschr. angew. Chem.*, 1890, 727.)

J. E. W.

ANALYSIS OF WINE.

The Determination of Sugar and Tannin in Wines.—Accurate results are not always obtained when Fehling's solution is used in determining sugar in wines, the cause being mainly that the coloring matter and tannin in the wines reduce more or less copper which is then calculated as if it were reduced by the sugar. The author as a test, made a solution of tannin containing 2 gr. to the litre. 25 cc. of this gave, when treated as if for a sugar determination, 0.0824 gr. Cu. equal to 1.702 per cent. sugar and from these figures concluded that 25 cc. of a 1% tannin solution gives copper from a Fehling solution equivalent to 0.91 per cent. sugar.

To study the influence of the coloring matter in wine on the sugar determination a sample of Portuguese wine called "Wine of Barrada" was taken. This wine contained 3.90 per cent. tannin and by the vinocolorimeter gave a violet red color, 63°.

A portion diluted 10 times with water still gave a dark red color and contained sugar equal to 1.606 per cent. A 1-10 dilution without removing the coloring matter or tannin gave sugar equal to 8.280 per cent. the sugar from the tannin being equal to 3.549 per cent. the coloring matter therefore caused an error of 3.125 per cent in the amount of sugar. In 200 cc. of this wine, when

digested with 50 gr. of animal charcoal for $\frac{1}{4}$ hour, there was an error of 2.32 per cent. and when 120 gr. charcoal was used the sugar found was 1.606 per cent.

From this it will be seen that the error caused by the coloring matter is often as much as 3 per cent. and more, and that by using finely pulverized animal charcoal and digesting for from 15 minutes to one hour, these errors are practically done away with.

For abnormally deep colors a much longer time is necessary for the digestion, but the author has found that as the absorption of the sugar by the charcoal, in most cases, is not more than 0.3 per cent., this will cause no great difference in the results.

The author looks upon the animal charcoal as a much better decolorizer than the acetate of lead, as from experiments given in his paper, he determines that results unavoidably high are given by this reagent.

For the estimation of the tannin in wines the author recommends Lowenthal's method in which the tannin is oxidized by potassium permanganate in a sulphuric acid solution in presence of indigocarmine and condemns the zinc acetate method which he says is absolutely unreliable. (J. H. Vogel, *Ztschr. Angew. Chem.* 1891, 44 and 69.)

J. E. W.

Volumetric Method for the Determination of Glycerine in Wines.

—The authors state that Pasteur was the first to discover the presence of glycerine in fermented liquids and to demonstrate that glucose under the action of ferments decomposes in the first place into carbonic acid and alcohol.



and as a secondary reaction in which water was decomposed gave



or succinic acid, glycerine and carbonic acid. Pasteur also came to the conclusion that 100 parts of cane sugar corresponding to 105.26 parts of glucose produced

Alcohol	51.11
Carbonic acid	49.32
Succinic acid	0.67
Glycerine	3.16
Matter given to the ferment	1.00

105.26

From this the proportion in general in wines should be 100 parts by weight of alcohol to 6.18 of glycerine.

This was found not to be the case in actual practice and the Imperial Commission of expert German Chemists, selected by the government to give its advice on the methods for the analysis of wines, in the session of 1884 established the proportion of 100 parts of alcohol to 7.14 parts of glycerine. Any wine containing more than 14 or less than 7 parts of glycerine to 100 of alcohol was to be considered as sophisticated.

The authors having been commissioned by the Italian Minister of Agriculture to make complete analyses of many samples of pure Sicilian wines, rejecting for various reasons the usual methods for the determination of glycerine in wines, propose the following method based on the property of glycerine to volatilize unchanged "in vacuo" at 180° C. and to be oxidized in an acid solution by permanganate of potash.

Two series of experiments were instituted: the first to establish the fact that all the glycerine was distilled over, and the second to determine the quantity of oxygen consumed by a given weight of glycerine and of what the products of the oxidation consisted. The glycerine used was chemically pure, and an ultimate analysis of it gave:

	1.	2.	Theory.
Carbon . .	39.15 per cent.	39.07 per cent.	39.13 per cent.
Hydrogen, 8.91 "		8.88 "	8.69 "

A quantity of this glycerine was dissolved in enough distilled water to give a solution of one part of glycerine per thousand.

10 cc. of this solution was carefully distilled from a tubulated glass retort, the neck of which ran through a Liebig condenser into a receiver, the latter being connected in turn with a Bunsen pump. The retort was heated in air bath kept at a temperature of about 200° C. To the distillate, transferred to a beaker, was added 5 cc. of sulphuric acid, and after heating to 100° C., one-tenth normal solution of permanganate of potash, drop by drop, with constant stirring, until a permanent rose color was obtained. The excess of permanganate was determined by one-tenth normal solution of oxalic acid.

Four determinations gave: 9.07 cc., 8.95 cc., 9.05 cc., 9.11 cc.

Mean, 9.04 cc. of one-tenth normal permanganate solution for each 10 cc. of glycerine solution.

Direct oxidation of the glycerine solution without distillation gave for 10 cc. of glycerine solution 9 cc., 9.03 cc., 9 cc. Mean, 9.01 cc. of the same permanganate solution.

From these determinations they conclude :

1. Glycerine in an aqueous solution is entirely distilled over at a temperature of 200° C. at very low pressure.

2. 0.01 gm. of glycerine requires for its oxidation 9 cc. of one-tenth normal permanganate solution, equivalent to about 0.0072 gm. of active oxygen.

To determine the nature of the reaction, the authors oxidized weighed quantities of glycerine with permanganate in the presence of sulphuric acid, at 100° C., and distilled the resulting solution. They found nothing but acetic acid, and quantitative determinations of the amount gave for 4.2672 gms. of glycerine 2.2195 gms. of acetic acid, from whence they deduce the equation.



To determine the amount of glycerine in wine, proceed as follows: Evaporate 10 to 15 cc. of wine on the water bath, adding distilled water from time to time, to keep the volume constant, until the alcohol is all volatilized. Treat the solution with acetate of lead, filter, and wash well. Precipitate the lead by carbonate of soda, filter, wash well, evaporate the filtrate on the water bath to about 15 or 20 cc., distill, and determine the glycerine in the distillate exactly as described above.

To test the accuracy of the method, the authors made a mixture of

Glycerine	0.10 gms.
Tannin	0.08 "
Bitartrate of potash	0.20 "
Acetic acid	0.10 "
Succinic acid	0.05 "
Glucose	1.00 "
Coloring matter	0.20 "

12 cc. of alcohol and enough distilled water to make a volume of 100 cc.

Using 10 cc. of this solution for each determination, they found

that there was required 9.05 cc., 9.15 cc., 9.02 cc., 9.17 cc. of one-tenth normal solution of permanganate, while the calculated amount was 8.695 cc., and the experiments with pure glycerine 9.025 cc. (V. Oliveri and M. Spica, Gazz. Chim. Ital. 1890, p. 773.)

A. A. B.

LEVOSIN—A NEW CARBOHYDRATE IN CEREALS.

Preparation.—The ground cereal is exhausted by alcohol of 50 per cent. and the extract treated with two volumes of alcohol of 94 per cent., which precipitates from it a large quantity of gum. After decantation, the liquid is distilled and to the residue from the distillation some solution of hydrate of barium is added until an additional quantity does not produce an additional precipitate which is immediately redissolved. The material is then filtered and into the clear liquid thus obtained a large excess of solution of barium hydrate, hot and concentrated, is added, until a permanent precipitate is formed. After cooling, the precipitate is collected, washed with cold hydrate of barium solution and afterward decomposed by carbonic acid. The carbonate of barium is separated from the hot solution and the levosin is obtained by evaporation, but containing still from .5 to 1 per cent. BaO. In purifying it, it is redissolved in the least possible quantity of alcohol at 60° and a little dilute sulphuric acid added in quantity just sufficient to precipitate the barium. The levosin is afterward precipitated by an excess of alcohol of 95 per cent.; it is then to be taken up by water, filtered and dried.

The composition of levosin, dried at 110 degrees, can be represented by the formula $C_{48}H_{80}O_{40}$. It has, indeed, the same percentage composition as starch and dextrine, and, by the method of Raoult, its molecular weight was found to be about 648. The dried compound, exposed to the air, takes up about 11 per cent. of its weight of water, which gives a definite hydrate containing four molecules of water for each molecule of the substance.

Levosin is a white body, amorphous and almost tasteless. It dissolves in water in all proportions; it is very soluble in weak alcohol, but is insoluble in alcohol of 95 per cent. It becomes soft at 145 degrees, but does not melt entirely until a temperature of 160 degrees is reached. Its specific gravity is 1.62. It is levogyrotory, whence the name proposed. Its specific rotatory power

is ($^{\circ}\text{D}$) = -36 . Its rotatory power does not vary with the period of solution, nor under the influence of temperature.

Levosin is not reduced by Fehling's solution, and does not ferment with yeast. Diastase has no action upon it. It suffers hydrolysis under the influence of very dilute acids with the same rapidity as cane sugar. It suffers also hydrolysis by heating in a sealed tube with distilled water at 100 degrees for 48 hours. Its rotatory power is then increased, and becomes ($^{\circ}\text{D}$) = -76 . It appears then to consist of a mixture of three-quarters levulose with one part of feebly dextrogenous glucose. Levosin is not attacked by alkaline solutions even when boiled. It forms definite compounds with bases, some of which have been analyzed. Levosin is not precipitated either with a neutral or basic acetate of lead, but is precipitated by lead in an alcohol solution. It is also precipitated by an ammoniacal solution of acetate of lead. Levosin is not only a polyglucoside, but it is also a polyatomic alcohol. Heated with anhydrous acetic acid and dry acetate of soda, it gives a triacetic ether, difficultly saponifiable, but from which the levosin can be recovered unaltered. If the acetate of soda is replaced by the chloride of zinc, a tetracetic ether is obtained. Dissolved in the cold in fuming nitric acid, levosin gives, by precipitation by sulphuric acid, a product easily explosive, the composition of which corresponds to a mixture of di- and tri-nitric ethers. Levosin is not colored by iodine. Nitric acid changes it into oxalic acid without intermediate formation of mucic acid.

Levosin has been found in rye, barley and wheat; it has not been found in oats, nor has it been detected in ripe maize. (Tanret, C. R., vol. 112, Feb. 2, 1891, pp. 293, et seq.) H. W. W.

GENERAL METHOD FOR THE ANALYSIS OF BRANDIES AND ALCOHOLS.

For the following determinations, except in the case of nitrogenous products, which are determined in the original sample, the distilled liquid, brought to the standard of 50° is to be used.

Ethers.—100 cc. of the distilled alcohol is boiled with 20 cc. of decinormal caustic potash for one hour, in a flask with an inverted

condenser, the amount of potash absorbed being determined from the acidity of the alcohol, and the results are calculated as ethyl acetate.

Aldehydes.—4 cc. of rosaniline bisulphite are added at the same time to 10 cc. of a solution of ethylic aldehyde (1 part in 10000) and to 10 cc. of the alcohol under examination (both at 50°). The tints are allowed to develop for twenty minutes, and a comparison of their intensity is made by means of the Dubose colorimeter, the dilution of the alcohol being repeated until the two tints match. If M represents this dilution, then $M \times 0.050$ will equal the weight of ethylic aldehyde per litre.

Higher Alcohols.—1 cc. of aniline and 1 cc. of phosphoric acid at 45° B. are added to 100 cc. of the distilled sample. The liquid is then boiled for an hour with an inverted condenser and afterward evaporated to dryness in a sand bath.

The distillate is treated with sulphuric acid at 66°, according to the known method, and the tint observed is compared with that given by an alcoholic solution containing 0.250 isobutylic alcohol per litre, and dilution is continued until the same tint is reached.

Nitrogenous Products.—The weight of ammonia, corresponding on the one hand to the amides and to saline ammonia, on the other to the pyridine bases and the alkaloids, is determined by treating the alcohol first with sodium carbonate, and then with alkaline permanganate and titrating the small amounts of ammonia produced in each case with Nessler's reagent. 2 cc. of phosphoric acid at 45° B. is added to 100 cc. of the original sample and the alcohol is expelled by boiling. The solution remaining is diluted with about 1 litre of distilled water. 10 gms. sodium carbonate are added, and the mixture is distilled till no more ammonia passes over. The permanganate and caustic potash are then added, and the distillation continued, the ammoniacal water being collected separately, and the amount of ammonia is determined with Nessler's reagent, comparing with a solution containing 0.00001 gms. ammonium chloride per 1 cc. (Ed. Mohler, Chem. News, 63, 111. Comptes Rendus.)

A. H. W.

QUANTITATIVE DETERMINATION OF FORMIC ACID IN THE PRESENCE OF ACETIC AND BUTYRIC ACID.

The author following the property observed by Portes and Ruysen (Comp. Rend. LXXXII p. 1504) of the reduction of mercuric chloride to mercurous chloride by formic acid proceed as follows: Weigh out a portion of the liquid containing the formate, transfer it to a beaker, add an excess of a saturated solution of mercuric chloride, cover with a watch-glass and heat for two hours on the water-bath. Filter on a weighed filter, wash with water at 60 C, dry at 100 and weigh the mercurous chloride. Should the liquid contain free formic, acetic and butyric acids, neutralize with caustic potassa before adding the mercuric chloride. The reaction is $\text{H.COOH} + \text{HgCl}_2 = \text{CO}_2 + 2\text{HCl} + 2\text{HgCl}$.

As the weight of the reduced mercurous chloride is more than ten times that of the formic acid, the test is a very sensitive one. Neither acetic nor butyric acid reduces mercuric chloride.

The test analyses given by the author are very satisfactory.—
A. Scala, Gazz. Chim. Italiana, 1890, p. 393. A. A. B.

THE RELATIONS OF MOLECULAR DISPERSION AND MOLECULAR WEIGHTS.

The relations of molecular dispersion and molecular weights have been investigated by Barbier and Roaux (C. R. 110, 527), and the formula constructed $\frac{M(B-b)}{p}$ in which M represents the molecular weight of the saline body in solution, B the increased dispersive power of the solution over b, the dispersive power of water, and p the saline matter dissolved. The formula represents the molecular increase in dispersive power. The constant K for each body is expressed in the formula:

$$B - b = Kp.$$

For chlorides of the type MCl, the mean increase is 0.020, and for MCl₂ 0.044.

Certain definite relations, therefore, subsist between molecular structure and dispersive power similar to those between refractive power and molecular weights described by Doumer (C. R., 110, 40.) H. W. W.

DETERMINATION OF CELLULOSE AND STARCH.

The apparatus used is an enlarged form of Anschütz's apparatus for melting point determinations, except that the inner vessel is not melted fast to the neck of the outer one.

2 gms. of the finely powdered substance to be analysed is placed in the tube with 60 cc. anhydrous glycerine and heated in the acid bath to 210° C. with occasional stirring. After cooling to 130° , the mixture is poured into a beaker and treated with 200 cc. 95 per cent. alcohol. The tube is carefully washed out with hot water, using a glass rod to remove any cellulose that may adhere to the sides, and the washings, which should not exceed 50 cc., are added to the main solution. When the solution has become perfectly cold, 50 cc. ether is added, and the whole is thoroughly mixed. The precipitate is then filtered, washed with alcohol and ether (5 : 2), and dried on a porous plate. When dry, it is heated in a flask on a water bath with 150 cc. water until the alcohol has been driven off. The flask is then connected with an inverted condenser, and 10 cc. hydrochloric acid (sp. gr. 1.125) is added to the solution and heated again on a water bath for half an hour. The cellulose is then collected on a tared filter and weighed. The filtrate is diluted to 250 cc., to which have been added 12 cc. hydrochloric acid (sp. gr. 1.125), and heated on a water bath, in a flask provided with an inverted condenser, for 3 hours. The resulting sugar is titrated with Fehling's solution. Duplicate results in wheat, corn, oats and barley differ from each other from .1 to .2 per cent. (M. Hönig, Chem. Zeit: 14, 868, 902.) s. c.

DETERMINATION OF TANNIN.

The following solutions are required :

An iodine solution, made by dissolving 5.2 gms. iodine and 7.6 gms. potassium iodide in water, and diluting to one liter.

A tannin solution, made by treating 1 gm. of pure dry tannin with water, and diluting to one liter.

A sodium bicarbonate solution, made by dissolving 100 gms. sodium bicarbonate in water and diluting to one liter.

Carbon bisulphide for an indicator.

The strength of the iodine solution is determined by placing 10 cc. of the tannin solution in a glass-stoppered flask and adding 20 cc. of sodium bicarbonate solution, 10 cc. water, and 2 or 3

cc. carbon bisulphide. The contents of the flask are thoroughly mixed by shaking, and iodine solution is run in from a burette until a violet color appears.

10 cc. of the solution to be examined (which should not contain more than $1-1\frac{1}{2}$ gm. tannin to the liter) is shaken with 30 cc. of sodium bicarbonate solution and 2 or 3 cc. carbon bisulphide, and then titrated with the iodine solution without taking into consideration any turbidity or precipitate that may be formed. The method is rapid, and gives good results. To determine the available tannin, the tannic acid in a second portion of the solution is precipitated with skin or lime, and the filtrate titrated with iodine solution as above. The difference in the titrations gives the amount of tannin in terms of iodine.

This method may be used for all astringent substances. The author has used it for tea, cider and wine. In wine, the coloring matter, as well as the different aldehydes, alcohols and other substances absorb the iodine. To overcome this difficulty, one determination is made in the usual manner, and in the other 50 cc. wine is well shaken with 50 cc. gelatine solution (2:1000) and filtered. 20 cc. of the filtrate (=10 cc. wine) is treated with 30 cc. sodium bicarbonate solution, and titrated with iodine solution. The difference in the titrations will give amount of cenotannin.

The albuminoids in wine may also be determined by this method. The wine is first titrated with iodine solution to determine the natural tannin. An excess of standard tannin solution is then added, which precipitates the albuminoids as an insoluble tannate. The excess of tannin is determined in the filtrate, and the percentage of albuminoids is calculated from the results. (A. Moullade, Chem. Zeit. Rep. 14, 251.) s. c.

ON THE ESTIMATION OF FAT IN MILK.

By series of 29 analyses the author shows the variable results obtained as to the percentage of fat in milk, when different methods are used.

The method he employed was Rose's—Soxhlet's areometric, and what is termed the sand or gypsum method.

Results by the sand method where the extraction was carried on for three hours, when compared with those by the Rose method

were found to be invariably lower, often as much as 0.19 per cent. By further extracting, an additional amount was obtained, and when carried on over night still more, thus showing that the length of time the extracting is continued, is a particular point in this method.

The mean difference between results obtained by seven hours extracting with the sand method and Rose's was $+0.068$ in favor of Rose's, while between the same and Soxhlet's areometric method the mean difference was $+0.015$ in favor of the latter, and between Rose's and Soxhlet's $+0.081$.

From the analyses the author decides, that in comparison with the sand and the areometric methods, Rose's method gives the best results, and that to obtain good results with the sand method the extracting must be carried on at least 6 or 8 hours for whole milk and for from 10 to 20 hours for skim milk, the areometric method while being extremely simple and rapid is not to be relied upon. (J. Gorodetzky, *Ztschr. Angew. chem.* 1890, 418.) J. E. W.

ON THE DETECTION AND SEPARATION OF MINUTE QUANTITIES OF HYDROGEN DIOXIDE AND URANIUM.

The author has detected .25 mg. of H_2O_2 by the following method: 1 to 2 cc. of ether are added to 5 cc. of a .005 per cent. solution of H_2O_2 (which contains .25 mg. of the dioxide), and then a small drop of a ten per cent. solution of chromic acid is added. After shaking well, and allowing the ether to collect, the blue color, due to the solution of the perchromic acid, is said to become quite distinct. By taking 1 cc. of a .01 per cent. solution of H_2O_2 , and proceeding in a similar manner, 0.1 mg. was detected.

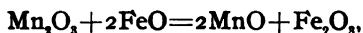
The reaction between salts of uranium and hydrogen dioxide has been made the basis for the separation and detection of uranium and the dioxide. In the absence of interfering agents, this process permits of the estimation of the dioxide by weighing the uranium precipitate, or by titrating it with permanganate. Dilute solutions of hydrogen dioxide and uranium nitrate were made, and 5 cc. of each was taken. A table is appended, showing that in very dilute solutions from $\frac{1}{20}$ to $\frac{1}{40}$ mg. H_2O_2 , and

from $\frac{1}{2}$ to $\frac{1}{4}$ mg. of uranium can be detected by this reaction.
(Thos. Fairley, Chem. News 62, 227.)

A. H. W.

VOLUMETRIC ESTIMATION OF MANGANESE.

The substance to be examined is dissolved, and the solution concentrated to 2 or 3 cc. 10 to 20 cc. of syrupy phosphoric acid (sp. gr. 1.95) are next added, then a few crystals of potassium chlorate, and the solution is heated gradually until all odor of chlorine is gone. The thick, syrupy liquid, after cooling, is dissolved in about 100 cc. water, and titrated directly by means of ferrous sulphate solution, or a solution of iron of known strength is added, and the excess titrated back with potassium permanganate. Considering the metals present as oxides, the reaction is



or 1 part Fe represents 1.4108 part Mn_2O_3 . Chromium must be absent, but cobalt does not interfere, provided all free chlorine is expelled before titration. In connection with phosphoric acid, it is stated that it is a powerful solvent for certain silicates, and it even attacks glass at a sufficiently high temperature. (Thomas Moore, Chem. News 63, 66.)

A. H. W.

NOTES.

The Sugar Beet in Wisconsin.—Under direction of Secretary Rusk of the Department of Agriculture, Washington, the Wisconsin Agricultural Experiment Station, at Madison, last season conducted experiments with sugar beets at the Station grounds and at five sub-stations in different parts of the state. In addition to this, beets received from seventy different farmers in the state were analyzed.

The six varieties of sugar beets grown at the Station contained from 14.81 to 16.76 per cent. of sugar in the juice; the coefficient of purity ranged from 82.2 to 86.3 per cent. About half an acre of each variety was grown, and the yield of washed beets varied with the different varieties from 16 to 26 tons per acre. The estimated yield of sugar varied from 2 to $3\frac{1}{2}$ tons per acre; in a well-managed factory about 80 per cent. of this quantity would be recovered as pure granulated sugar.

A careful account of the work done in planting and cultivating the plats of sugar beets grown, showed that it cost from 84 cents to \$1.38 to grow a ton of beets. This does not include the cost of harvesting and delivery, which may be considered as about equal to that of growing the crop.

The beet culture at five sub-stations gave beets whose sugar contents ranged from 12.81 to 17.14 per cent. of sugar in the juice, while the beets would have yielded from 4 tons (at the St. Croix county station, where wet cold weather in June caused the beets to rot and greatly reduced the yield,) to nearly 39 tons per acre. The latter heavy yield was estimated from the plants grown at the Waukesha Co. station.

Seventy farmers in 29 counties of the state sent samples of sugar beets grown by them to the Station for analysis. The results of the analyses showed a very wide range, according to the kind of seed used, the manner of growing, skill of the grower, etc; the lowest of all analyses showed 6.48 per cent. and the highest 18.79 per cent. of sugar in the juice. The latter result was obtained from beets grown near New Holstein, Calumet Co., from which locality also other samples were obtained containing a very high percentage of sugar, indicating that this section may prove particularly well adapted to sugar beet culture. Of other sections that seem well suited to this crop may be mentioned the counties of Kewaunee, Washington, Rock, Jefferson, Waukesha, Milwaukee, in short the whole eastern and southeastern portion of the state.

A New Solvent for Cellulose.—By dissolving in concentrated hydrochloric acid one-half its weight of zinc chloride, a solution is obtained (sp. gr. 1.44) which dissolves cellulose at once and without sensible modification. The reagent promises to be useful in the microscopic study of the vegetable fibres, structural peculiarities being clearly brought out under the microscope by the action of the new solvent. (C. F. Gross and E. J. Bevan, Chem. News 63, 66.)

A. H. W.

A Model Laboratory.—The new Laboratory Building of Messrs. Booth, Garrett & Blair, 406 Locust St., Phila., is well worth a visit from those who contemplate building. The laboratory

building is three stories in height and is of brick with concrete floors. The building is therefore fire-proof; it is lighted by means of a dynamo run by a gas engine and with a storage-battery of 25 cells for reserve power. The current also forms a convenient and cheap source of power for running the blower, stirring solutions, etc. The second and third floors which form the laboratory proper are well fitted up and supplied with all sorts of time and labor saving devices. The floor surface of these two floors is over 2500 square feet. The best feature of the establishment, however, is in the chemists Messrs. Thomas H. Garrett, Andrew A. Blair, George B. Garrett and J. Edward Whitfield, who occupy it. These gentlemen are well known, and belong to that class of men who mix brains with their work.

E. H.

The Detection of Coniine.—Andrews recommends that in poisoning cases the nature of the alkaloid be ascertained by a molecular weight determination as well as by qualitative tests. In a case which he examined coniine hydrochloride was separated and the amount of chlorine determined by Mohr's method with 3-100 silver nitrate solution. "The investigations of recent years concerning ptomaines have greatly complicated the labors of the toxicologist and increased the chances of escape of the criminal by enabling him to ascribe the observed reactions of an isolated poison to some hypothetical ptomaine."—*Am. Chem. Jour.* 13, 123.

E. H.

Notes on Platinum.—Messrs. Eimer & Amend have circulated among their customers a little pamphlet with the above title containing hints on the care of platinum vessels which are admirable and worthy of being put in the hands of every student beginning quantitative analysis.

Personals.—Mr. L. D. Godshall has been appointed Superintendent of the Holden Smelting Co., Denver, Col.

Mr. Geo. Faunce has been appointed Superintendent of the Penna. Lead Co., and Mr. Geo. A. Marsh, Assistant Superintendent.

NEW BOOKS.

*Erdmann's Chemischer Präparate.**—Dr. Erdmann has provided

*Anleitung zur Darstellung Chemischer Präparate von Dr. Hugo Erdmann, Privatdozent an der Universität Halle. Published by H. Bechold, Frankfurt. a. M. 1891.

teachers and students of chemistry with an admirable little book of directions for the preparation of inorganic compounds. To students that have already an acquaintance with the elements of the science, and some practice in laboratory work, a course of instruction in the preparation of compounds on a larger scale than that usually employed in elementary work is of very great value. This is especially the case if the student intends to do advanced work in the science. By a proper selection of the substances to be thus prepared it is possible to give him an opportunity to become familiar with a large number of important chemical transformations, as well as with the methods and the apparatus used in advanced work. There are several good books of directions for the preparation of organic compounds which are of service to the student and lighten the work of the teachers, and Dr. Erdmann deserves our thanks for having given us a similar one in the field of inorganic chemistry.

An examination of the book shows that the directions are clear and concise, and the reactions involved in each method are briefly explained. The selection of compounds to be prepared is well made. Every important element is represented by several characteristic compounds, and many of the methods given have originated in Professor Volhard's laboratory at Halle and are here published for the first time. Another feature of the book is that in many cases the raw materials used as the starting points for the preparation of the compounds are inexpensive substances, such as by-products, residues, etc., that accumulate in laboratories, while the finished products are substances that are frequently used in analytical and synthetical processes and which often can not be purchased in a condition of sufficient purity. The appendix contains valuable directions concerning certain indispensable laboratory appliances, such as gas burners, crucible furnaces, gas generators, etc.

On the whole it is an excellent little book and we heartily recommend it to teachers and students of chemistry. E. H. K.

THE

Journal of Analytical AND Applied Chemistry.

THE PIERCE PROCESS FOR THE PRODUCTION OF CHARCOAL, WOOD ALCOHOL, AND ACETIC ACID.

BY WM. L. DUDLEY.

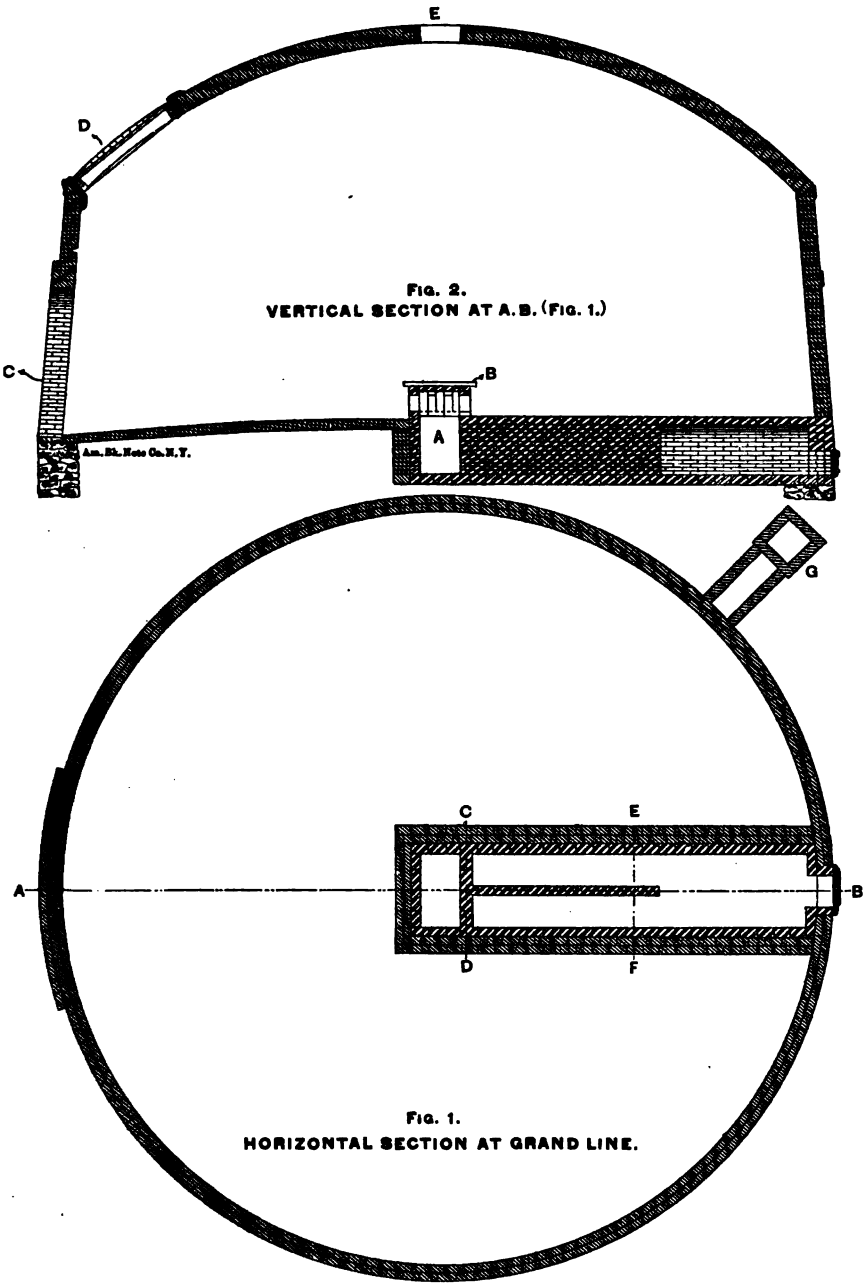
The rapid destruction of forests and the large and increasing demand for charcoal, makes an economical method for its production a necessity. The old methods are wasteful, not only on account of the consumption of a considerable amount of the wood in charring, but because of the loss of the bye products, namely, the combustible gas, tar, alcohol and acetic acid. The Pierce process, which was devised in its original form in 1876, in its present state of perfection certainly fulfills all of the demands in these particulars, and besides, it may be operated on a scale so large, and in such a simple manner, that the greatest possible economy can be obtained. One more point in its favor is the superior quality of the charcoal, which is of a grade much better than that made by any of the old methods. While it is undoubtedly possible to improve this process mechanically, it certainly seems to be a near approach to perfection from the standpoint of chemical technology. There are numerous plants operating this process. In 1888 nine of these plants consumed 325,000 cords of wood, the charcoal being used in making iron.

The process is briefly as follows :

The wood is stacked in brick kilns, which are heated by the combustion of the permanent gases produced by the destructive distillation of the wood going on in the other kilns in the battery.

All of the products of the destructive distillation of the wood are drawn from the kilns by an exhaust fan into a large main, and thence through a series of condensers, where the alcohol, acetic acid and tar are deposited. The incondensable gases are then forced back under the kilns, where they are mixed with air and burned in suitable furnaces. The products of combustion of these gases pass directly into the kiln, and are mingled with the products of destructive distillation of the wood, and continue on in the same cycle to condensers and back again to the kilns. The carbon dioxide produced by the combustion of the gases in the furnace is, of course, reduced to carbon monoxide, and the water formed in the combustion is decomposed, on passing through the mass of red-hot charcoal in the kiln; thus they are converted into combustible gases, and the combustibility of the products of destructive distillation is not impaired. In this way more gas is accumulated than is needed for carbonizing, and this excess is used under the boilers which supply steam to the engines driving the circulating fans, hoisting machinery, and also to the stills, etc., in the alcohol house. Even with this enormous consumption of gas, there is usually considerable to spare. The wood in the kilns is, at any one time, in various stages of carbonization. While some kilns are being charged, others are burning and others are being emptied. The liquor from the condensers is allowed to stand in tanks, where the tar settles, and the liquor containing the alcohol and acid is drawn off and neutralized with milk of lime. The neutralized liquor is run into the "primary" still; this distillate is redistilled in the secondary or "intermediate" still, and rectified in the final or "shipping" still. The residual liquor in the primary still, after distilling off the alcohol, is withdrawn, evaporated, and the crude calcium acetate is put on the market.

I will now give a more detailed description of the plant and process. The kilns are of the bee-hive form, 32 feet in diameter, 10 feet high to the springing line of the arch which has 6 feet rise to the crown, making the height of the kiln in the center 16 feet. The walls are 8 inches thick, except at A (Fig. 1), where they are 12 inches thick; at this point a charging door C (Fig. 2), 6 feet high and 5 feet wide, is cut.



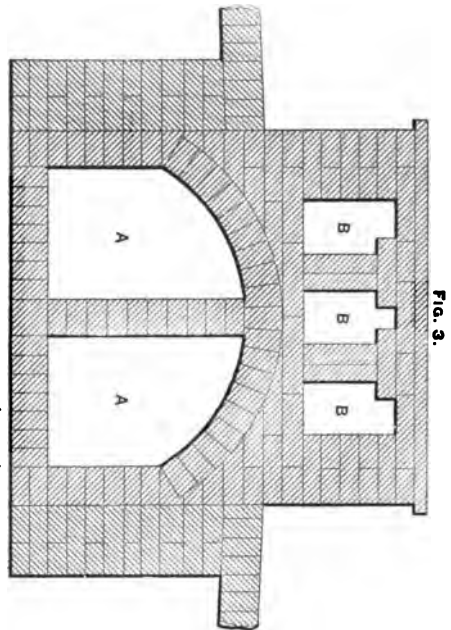
Under the floor of the kiln is the furnace C, D, E, F (Fig. 1), which is 3 feet wide and 2 feet high, extending from the outside of the kiln to a chamber A (Fig. 2), called the "heat distributor," in the center of, and opening into the kiln through the floor. This chamber is 20 inches wide by 36 inches long, and is covered by an iron plate B (Fig. 2), 2 inches thick and 48 inches square. Spaces are left in the brick walls under this plate, so as to admit the products of the combustion of the gases in the furnace directly into the kiln. These spaces are $6\frac{1}{2}$ by 11 inches in dimensions.

The furnace is divided through part of its length into two flues by a partition wall, as shown in Fig. 1. The chimney, for the exit of the gaseous products, is shown in horizontal section at G (Fig. 1); C and D (Fig. 2), are charging doors, D being used when the wood has been stacked in so as to make C impassable.

The charcoal is removed through the door C. These doors are of iron, and are securely held in place by iron bars fastened in projecting hooks. The circular opening E (Fig. 2), in the top of the kiln, is for light and ventilation while charging and discharging. During the burning it is covered by an iron plate.

Fig. 3 shows the cross section of the heat distributor at C, D (Fig. 1). AA are the flues of the furnace. The width of each flue is 1 foot 4 inches, and the height 2 feet, and 1 foot 4 inches at the division wall and side respectively. The "ports" or spaces through which the heated gases pass into the kiln are shown at B, B, B.

Fig. 4 is a cross-section at E, F (Fig. 1), showing the relative positions of the kiln floor and the roof of the furnace which projects higher above the former as it approaches the side of the kiln owing to the rise of the arch of the floor. The front elevation of the furnace is shown in Fig. 5. The inside dimensions of the door frame are 12 inches by 16 inches. This door is used only when the plant is first put in operation, for then, of course, there is no gas supply; or when an accident cuts off the supply during the burning of the kiln. The rest of the time this door is sealed up. A is the tuyere hole through which the tuyere injecting the combustible gases and air is introduced. Its diameter is 5 inches.



CROSS SECTION AT C D (Fig. 1.)

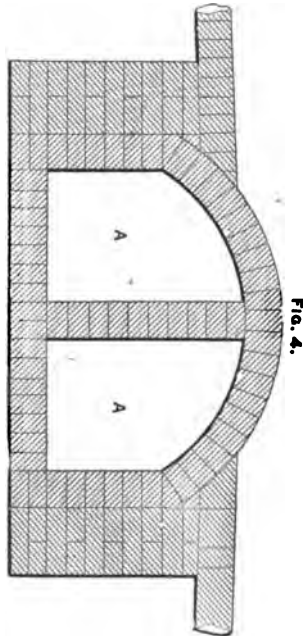
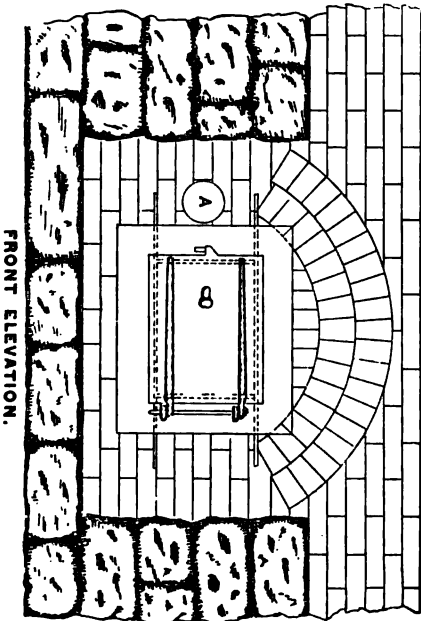


Fig. 4.

CROSS SECTION AT E F (Fig. 1.)

Fig. 5.



FRONT ELEVATION.

PLAN AND ELEVATION, SHOWING
ARRANGEMENT OF KILNS, GAS METRES, ETC.

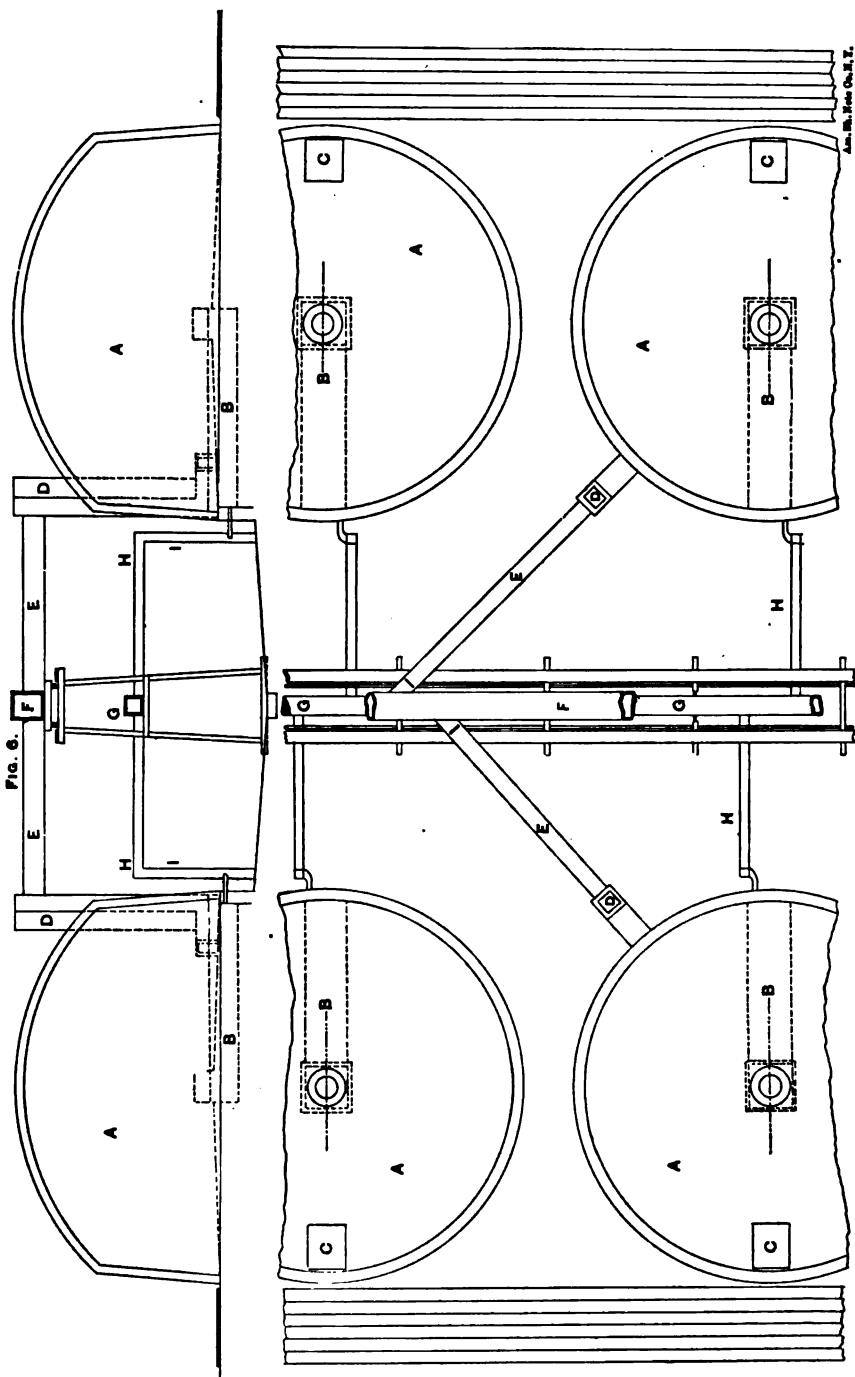
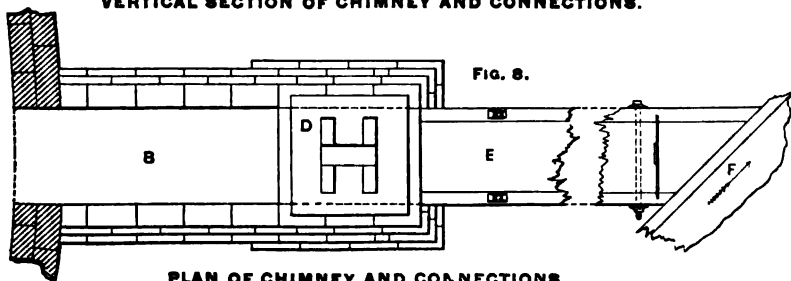
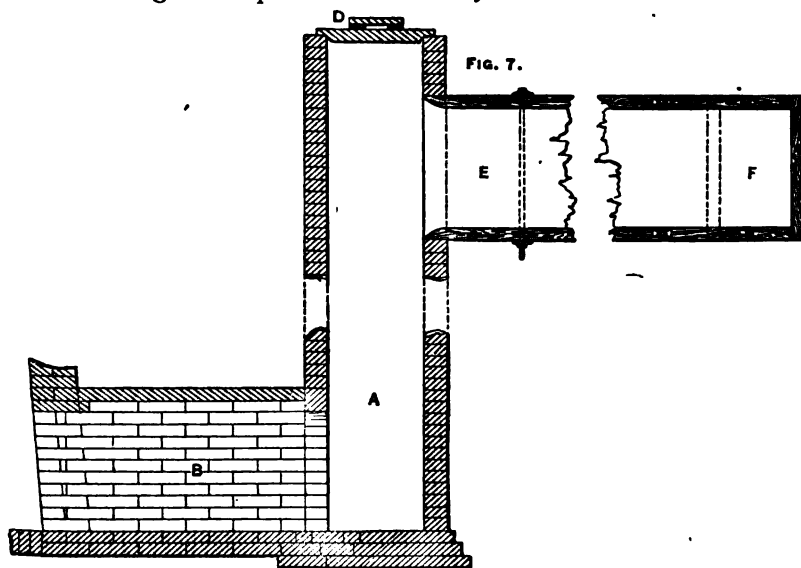


Fig. 6 is a plan and sectional elevation, showing the arrangement of the kilns and gas mains. A are kilns; B, furnaces; C, upper charging doors; D, chimneys; E, flues conveying the products of destructive distillation to the suction main F, which conveys them to the condensers; G, is the return main conveying the in-condensable gases back to be burned in the furnaces, to which they are led by the pipes H, and the "down-comers" I. The suction main F, pitches slightly toward the condensers, so that any liquor condensed *en route* will flow into tanks provided for it.

The chimney A (Fig. 7), which is 16 feet high and 16 inches square, is connected with the kiln by a horizontal flue B, 48 inches long, 16 inches wide by 20 inches high in the center and 16 inches high on the sides. The top of the chimney is 12 inches above the flue E which leads to the suction main F. D is a wooden cover. Fig. 8 is a plan of the chimney and its connections.



The gas flues and mains are made of plank, tarred and bolted together. The flues E (Fig. 6), are 12 inches by 20 inches. The suction main F is 22 by 24 inches; and the return gas main G is 13 by 14 inches. The flues H are 8 by 10 inches, and the "down-comers" I are 6 by 6 inches.

The condensers are wooden boxes 4 feet 4 inches square and 17 feet high, containing 99 copper tubes 2 inches in diameter and 14 feet long. These tubes or flues are fastened into flue-sheets AA (Fig. 9). A partition B, like a curtain, extends from the top of the condenser to within 2 feet of the bottom flue-sheet. This curtain deflects downward, the gas upon entering, and secures an exit at the opposite side near the top, convenient for entrance into the next condenser. The water which has been used in the succeeding condensers is brought into the box C, whence it falls through the tubes into D, thence passes up through the tubes on the opposite side into E, and thence to another condenser. The gas occupies the space outside of and between the tubes, and the current is in a direction opposite to that of the water, as shown by the arrows. The condensed products fall upon the lower flue-sheet, and are trapped off at F into the copper pipe G, which leads to the liquor tanks. Five of these condensers are connected in series. The gases from the suction main are drawn through the first condenser, whence they pass through the exhaust fan and are forced through the second, third, fourth and fifth condensers in succession. The plan of a condenser is shown in Fig. 10. A plant comprising 40 to 50 kilns would require at least two series of condensers.

After leaving the condensers the gases are brought into a "return gas receiver," which is a wooden box 4 feet 6 inches square and 10 feet high. From this receiver the gas is distributed through the return gas mains to the kilns, boilers, etc. On the top of the "receiver" is a "bleeder" or waste-gas escape pipe 12 by 15 by 12 inches high, closed by a hinged wooden valve worked by a rope over a pulley.

On returning to the kiln, the gases are injected into the furnace by a jet of steam issuing from a nozzle, having a one-sixteenth inch orifice, fixed in the center of a 1 inch copper pipe connected with the "down-comer." This copper pipe passes into the tuyere hole of the furnace at which point also, sufficient air is admitted to afford complete combustion.

The operation of the plant is as follows : the cord-wood is stacked vertically in the kilns, layer upon layer, as high as possible, and the unoccupied space at the top is filled by sticks placed horizon-

FIG. 9.
CONDENSER.

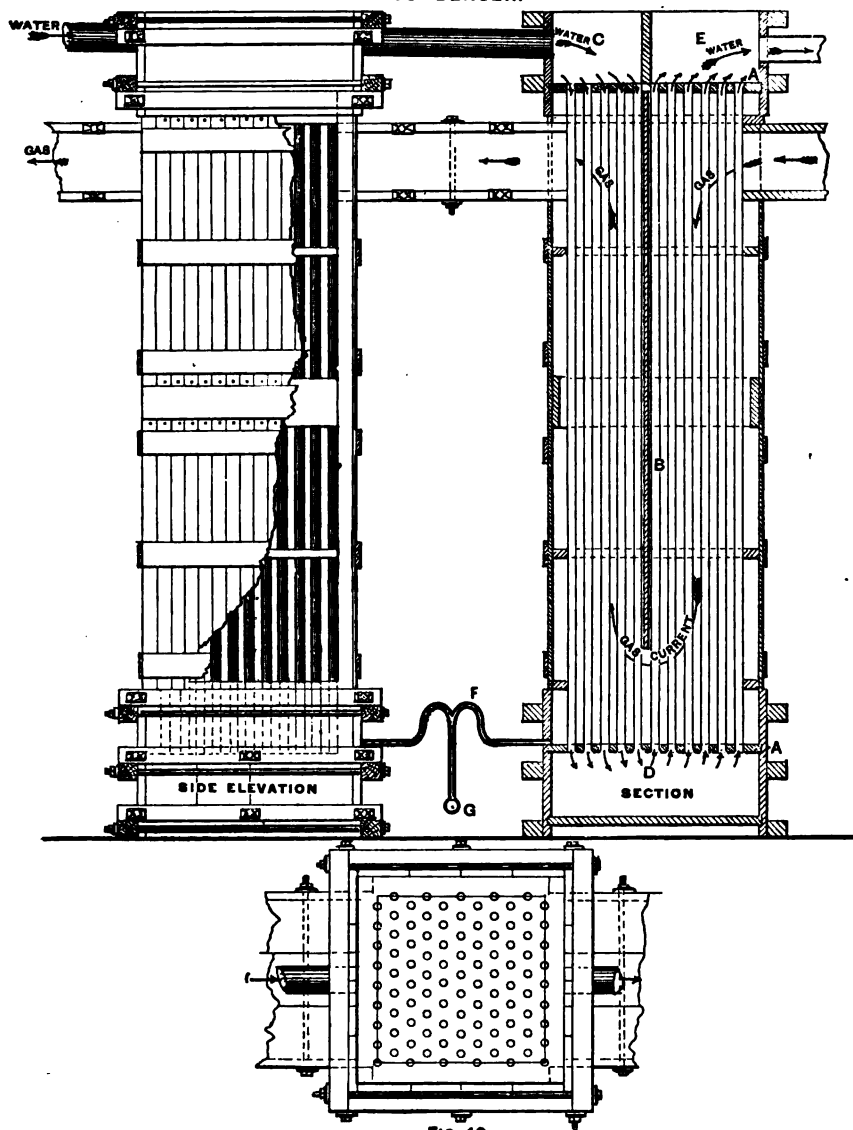


FIG. 10.
PLAN OF CONDENSER.

tally. The iron doors are fastened in place and tightly luted with clay. A lighted torch is introduced into the furnace, or a fire is kindled with a few sticks of wood, and the gas is turned on. The valve in the flue connecting with the suction main remains closed, and the cap on the top of the chimney is removed. The "seasoning" or drying out of the wood in the kiln then begins, the steam issuing from the chimney. The drying out begins with the wood directly over the "heat distributor" and proceeds in a vertical column to the top of the kiln, and then proceeds from the top downward. The charring proceeds in the same manner. In from 12 to 18 hours the white vapor issuing from the chimney is succeeded by a pale bluish smoke, which is a signal that the charring has begun. The valve connecting with the suction main is now opened and the cap replaced on the top of the chimney. The charring is completed in from six to eight days. At the end of this time the valves in the "down-comer" and suction flue are closed, and the hermetically sealed kiln is allowed to cool, which requires about six days. Allowing two days for filling and two days for drawing the charcoal, the whole operation of burning one kiln will have taken eighteen days, and fifty-five cords of wood will have been charred. In a plant of 48 kilns, the following schedule will show the state in which they will be found at any one time :

5 kilns are being charged and closed.
 3 kilns are being seasoned.
 15 kilns are being carbonized.
 13 kilns are being cooled.
 5 kilns are being drawn.
 7 kilns are idle for repairs or acting as relays.

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After each burning, the kiln is coated heavily on the outside with thick whitewash, which closes all the seams and small cracks caused by the expansion and contraction of the walls.

The following figures, which I have taken from a paper by Prof. O. H. Landreth, entitled "The Economical Production of Charcoal for Blast Furnace Purposes,"* will be found interesting :

The average ratio by weight of charcoal to wood in U. S.	18 per cent.
" " " " " " France	19 "
" " " " " " Belgium	16 "
" " " " " " Pyrenees	17 "

The resulting general average in above countries 17.5 "

The average ratio by weight of charcoal to wood by Pierce Process 25.3 "

*Abstract in Proc. A. A. A. S., 1888, p. 145.

The average ratio by weight of charcoal to wood by laboratory distillation	25.6	"
The resulting ratio of increase of Pierce process over average practice in the above mentioned countries	44.	"
The resulting ratio of increase of Pierce process over average practice in U. S.	33.	"

The quantitative values of the products resulting from the destructive distillation of wood by the Pierce process are as follows :

Dry Wood.	1 Cord.		4000 lbs.		100%
Resulting Charcoal . . .	50.6 bush.	1012 lbs.		25.3 %	
Methyl alcohol . . .	4.4 gals.	30 "		0.75 %	
Acetic acid . . .	4.6 "	40 "		1.0 %	
Tar	16.5 "	160 "		4.0 %	
Water	220.7 "	1838 "		45.95 %	
Incondensable	11000.00				
Gases	cu. ft.	920 "		23.0 %	
		4000 lbs.	4000 lbs.	100.0 %	100%

The condensed products are conveyed to tanks where the tar is deposited and drawn off at the bottom. The liquor containing the alcohol and acid is pumped up into storage tanks along side of the alcohol house. The tar is mostly used for painting the gas mains, condensers, etc.

From the storage tanks the liquor is conveyed to the neutralizing tanks which are 3 feet high and 7 feet in diameter, made of wood. Each of these tanks contains a stirrer consisting of four wooden paddles fixed on a vertical axis having a handle outside. Lime and water are mixed in a small circular tank and run into the acid liquor which is agitated by the revolving stirrer. The neutral point is determined by removing samples from time to time and testing for free acid.

The neutralized liquor is run through the pipe A into the primary still, which is shown in Fig. 11. The still is 8 feet in diameter at the bottom, 6 feet 9 inches at the top and 7 feet 1 inch high. It is made of wood bound by iron hoops. The liquor is heated by the steam coil B which is made of 2 inch copper pipe. "Live" steam is admitted into the still through the pipe C, when it is desired to hasten the heating of the liquor. The vapors pass into the dome D, and through the pipe E into the "cooler." The calcium acetate liquor is drawn off through F and conveyed to the "acetate liquor tanks," while any residue which may have been formed is removed through G.

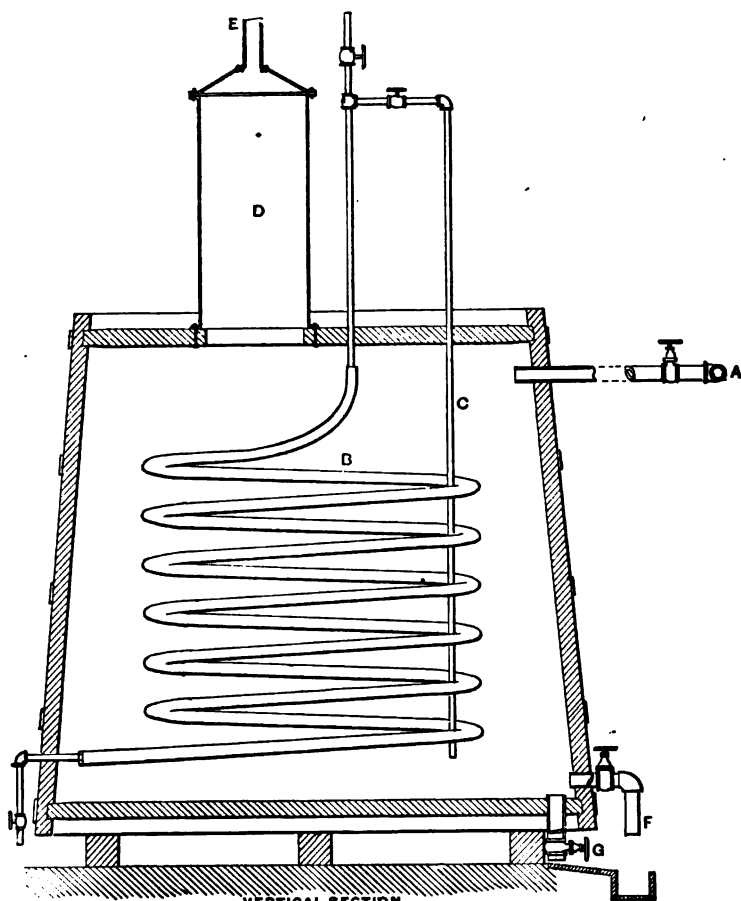
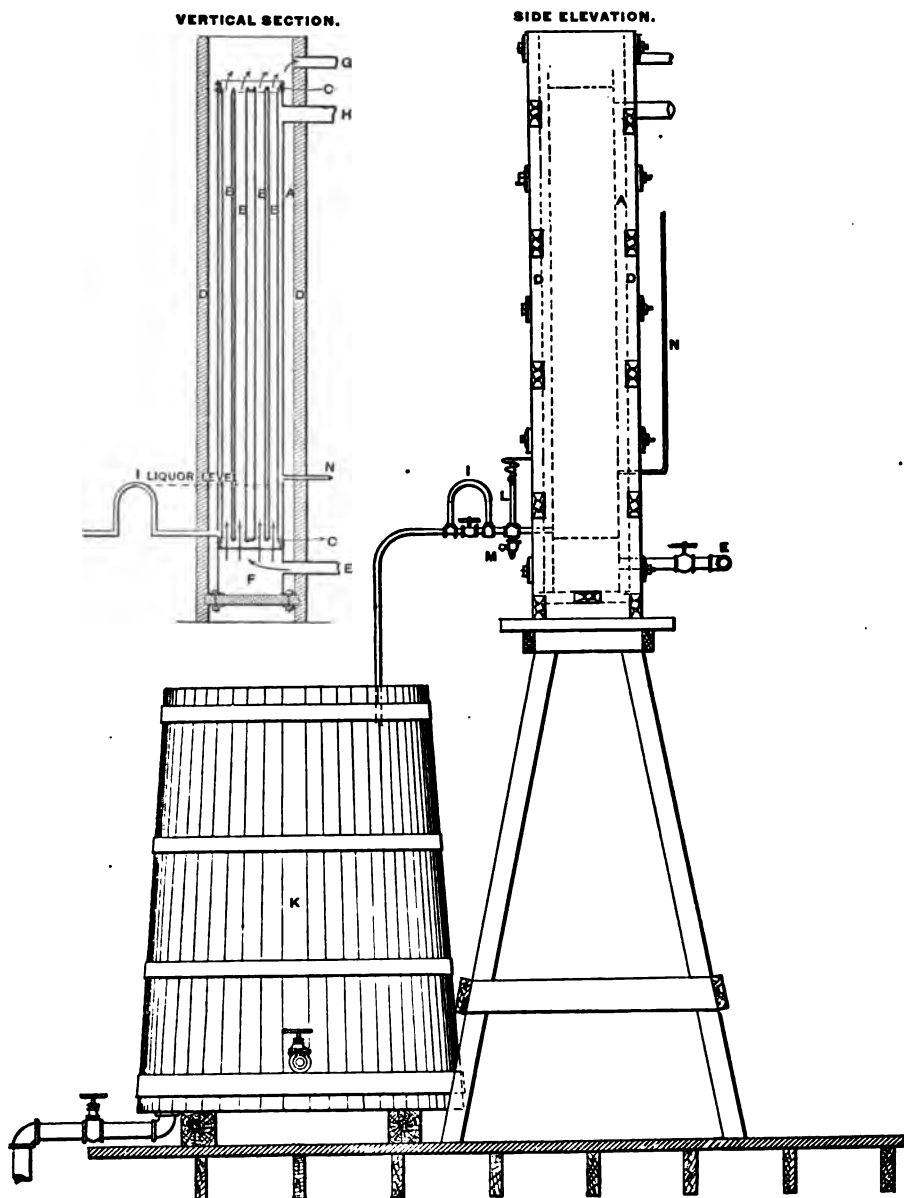


Fig. 11. -- PRIMARY STILL

The alcoholic vapors from the primary still are conveyed to the "cooler" Fig. 12, which consists of a copper cylinder A, 1 foot in diameter and 7 feet 10 inches high, containing 14, 2 inch copper tubes BB, open at both ends, and fixed in the tube sheets CC. Surrounding this copper cylinder is the water-tight wooden box D. The cooling water enters through the pipe E into the chamber F at the bottom of the copper cylinder and passes up through the tubes BB, and escapes through the pipe G. The water also surrounds the copper cylinder. The alcoholic vapors from the still enter the copper cylinder through the copper pipe H and passing around and between the cool tubes is condensed and trapped off at I into the tank K. L is a glass tube which serves as a gauge,

and samples for testing are withdrawn at M. N is a "vapor pipe," 4 feet long, which allows the air and other permanent gases to escape, thus preventing the accumulation of pressure.



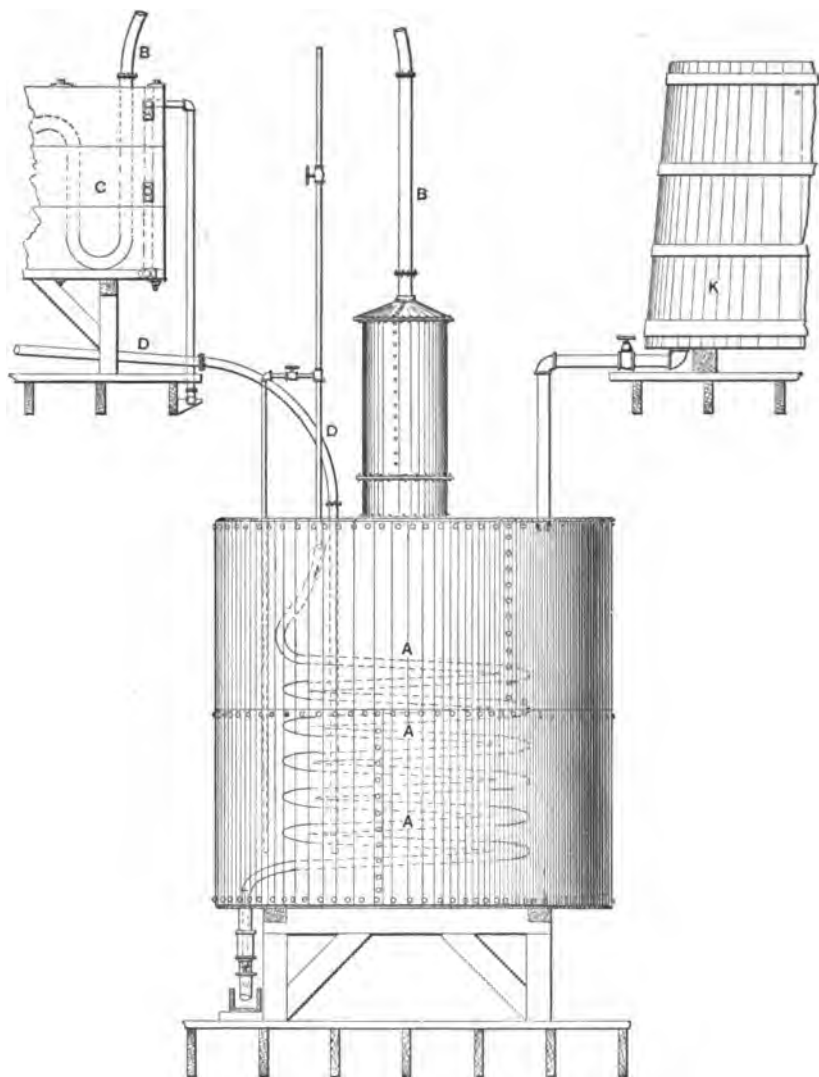
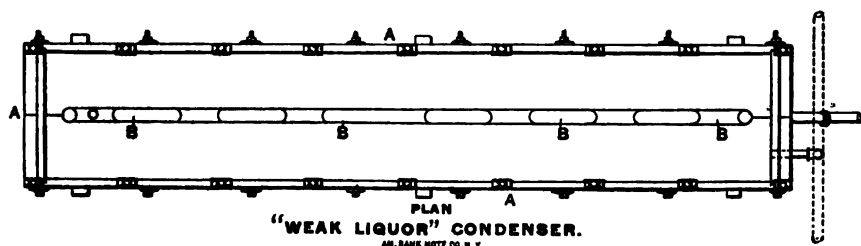
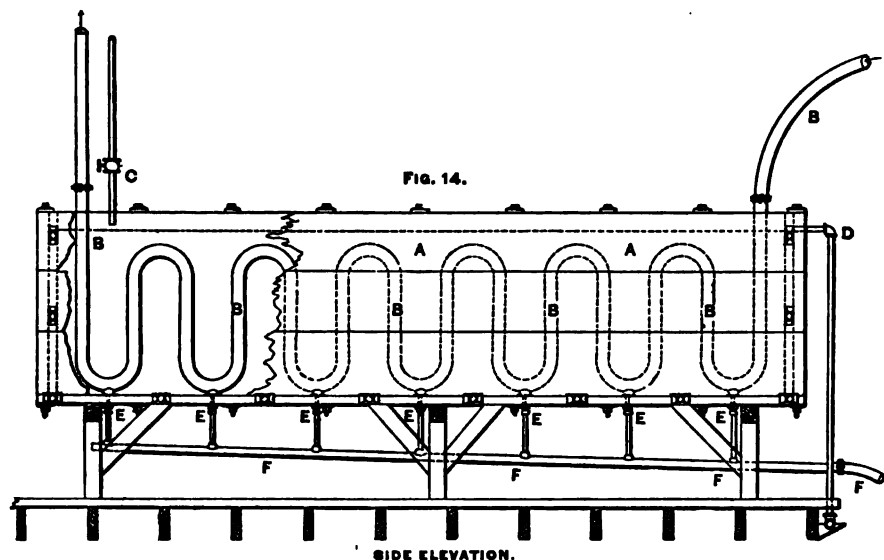


FIG. 13.

INTERMEDIATE STILL.

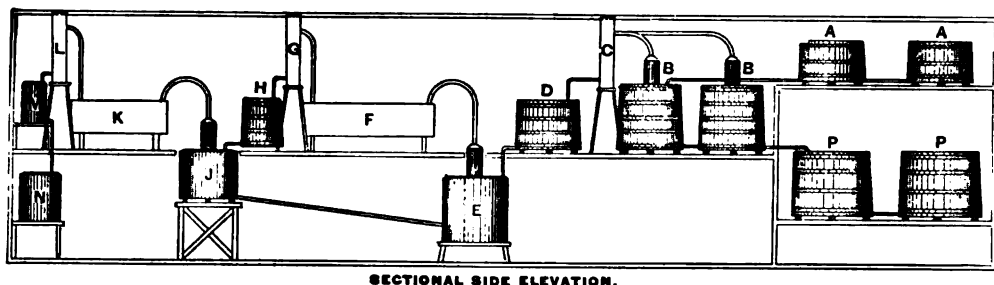
From the tank K (Figs. 12 and 13), the liquor is run into the secondary or "intermediate" still Fig. 13, which is 5 feet in diameter and 8 feet high, and made of boiler iron. It is heated by the steam coil A. The vapor passes through the pipe B, into the "weak-liquor" condenser C. The "weak-liquor" is returned to the still through the pipe D.

The "weak-liquor" condenser consists of a water-tight wooden trough A (Fig. 14), 16 feet long, 3 feet wide and 4 feet deep, into which the pipe B from the "intermediate" still carrying the alcoholic vapor, passes and makes a series of vertical U shaped bends. The condensing water which has passed through the "cooler" enters the trough A through the pipe C, and passes out at the opposite end through D. The condensing water is maintained at from 80° C. to 95° C., thus condensing most of the vapor of water, with of course some alcohol, in the pipe B. This weak liquor flows to the bottom of the U shaped bends and through the pipes E runs into F and thence back into the "intermediate" still. The uncondensed alcohol passes on through B to a "cooler" of the same construction as that already described



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and shown in Fig. 12, and from thence the alcohol passes into the "intermediate liquor" tank. From this tank the liquor passes into the final or "shipping" still which is similar in construction and design to the "intermediate" still, but is smaller; being 6 feet high and 6 feet 6 inches in diameter. The distillate is condensed in a "weak-liquor" condenser and a "cooler" similar to those already described.



SECTIONAL SIDE ELEVATION.

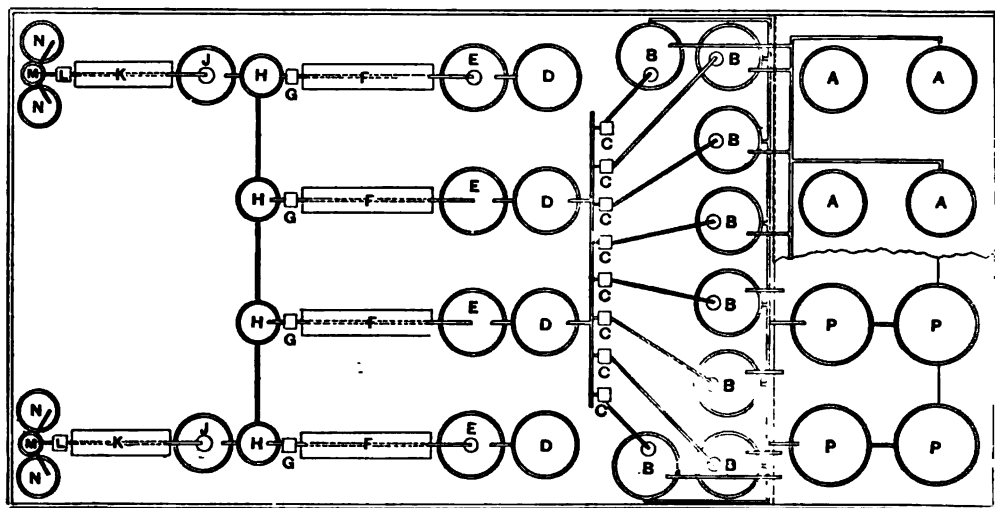


Fig. 15.--ALCOHOL HOUSE.

The alcohol house usually contains eight "primary," four "intermediate," and two "shipping" stills. The following table shows the alcoholic strength of the liquors at the end of each distillation :

Liquor entering the primary stills . . .	1.5 per cent. alcohol.
Distillate from " " . . .	15.0 " "
" " the intermediate " . . .	42.0 " "
" " the final " . . .	82.0 " "

Frequently the final distillate runs as high as 90 per cent. alcohol, in which case it is diluted to 82 per cent. for shipment.

Fig. 15 gives a plan, and sectional side elevation of the alcohol house showing the arrangement of the tanks, stills, condensers, coolers, etc. A are neutralizing tanks; B, primary stills; C, primary coolers; D, primary liquor tanks; E, intermediate stills; F, intermediate weak-liquor condensers; G, intermediate coolers; H, intermediate liquor tanks; J, final stills; K, final weak-liquor condensers; L, final coolers; M, final liquor tanks; N, shipping storage tanks; P, acetate liquor tanks.

Fig. 16 is a plan of a complete plant, comprising 48 kilns arranged in three batteries of sixteen each.

VANDERBILT UNIVERSITY.

Feb. 19, 1891

NOTES ON THE ESTIMATION OF NITROGEN IN NITRATES BY KJELDAHL'S METHOD, AND AN INDEX TO THE LITERATURE ON THE ESTIMATION OF NITROGEN.

BY LYMAN F. KEBLER.

In the history of analytical chemistry, no method has been so universally adopted, in so short a time, as the "Kjeldahl Method" for the estimation of nitrogen. The fundamental reactions in the method, according to Dafert,* are as follows: First, The sulphuric acid abstracts from the nitrogenous organic material, the elements of water and ammonia gas, forming ammonium hydrate, and subsequently ammonium sulphate; Second, The sulphurous anhydride which is evolved reduces the nitrogenous compounds, but this is insignificant as compared with the first reaction.

The original method is not applicable for the estimation of nitrogen in all inorganic and organic combinations; but the

*Ztschr. anal. Chem. 1888, 27, 222.

method has been modified to such an extent that the nitrogen in almost all inorganic and organic combinations can be estimated by it.

The method, as followed by the writer, is given in detail in Bulletins Nos. 19 and 24 of the U. S. Agricultural Department.

The instructions which were followed did not indicate how the distillate should be received in the receptacle.

After making a series of experiments, the writer found it necessary to connect the end of the condenser with the receptacle by a glass tube dipping below the liquid contained in the receiving flask.

While working with this method, the writer observed, that whenever the sulphuric acid was added to some material containing nitrates, nitric acid was evolved, and could be detected by its odor at the mouth of the flask. It was plainly evident that this must be overcome in some way. It was observed that when the sulphuric acid was added quickly and the flask shaken moderately, none, or very little, of the nitric acid escaped from the sulphuric acid; none escaped from the flask.

After this observation, a series of experiments were made, with the following results:

1st. The sulphuric acid was added slowly in *eight** different experiments, when the maximum amount of nitrogen obtained was 16.03 per cent.; minimum, 15.91 per cent.; average, 15.97 per cent.

2nd. The sulphuric acid was added quickly in *twenty-six* different experiments, when the maximum amount of nitrogen obtained was 16.33 per cent.; minimum, 16.03 per cent.; average, 16.18 per cent.

The smaller the quantity of material employed, the greater the percentage obtained. In the above experiments as uniform a quantity of material as possible was employed.

If the sulphuric acid converts the nitrogen into ammonia, why add the potassium permanganate? From a large series of experiments, the writer concludes with Lenz,† that the potassium per-

*The work was all done on sodium nitrate.

†Ztschr. anal. Chem. 1887, 26, 590.

manganate when added to a hot mixture destroys the organic compounds still remaining, and if the digestion is carried far enough all of the nitrogen is then converted into ammonia.

Of what value is the addition of metallic oxides or metals? The time consumed for complete oxidation when a metal or metallic oxide was added varied from *two to four hours*, while without the addition of these from *ten to thirty hours* were required for complete oxidation. In order that a method be practicable, its execution must require as little time as possible.

During the first part of my work, to prevent bumping, metallic zinc was used, but was soon found to be entirely unnecessary, especially when a Fletcher's circular burner was employed.

The results obtained by Kjeldahl's method were found by the writer to be a trifle lower than those obtained by the absolute method; agreeing very closely with those of Ruffle's method. The absolute method yielded, from *twelve* combustions, an average of 16.28 per cent., while the Ruffle's method yielded, from *ten* combustions, an average of 16.16 per cent. By comparing the above results, it was concluded :

1. The Kjeldahl method is not as accurate as the absolute method for estimating nitrogen in nitrates, but is executed in much less time, since many estimations can be made at the same time, and is applicable for all practical purposes.

2. It is necessary to add the sulphuric acid quickly, that there may be no loss of nitric acid.

3. The end of the condenser must dip into the liquid contained in the receiver.

4. In order to economize time, a metal or metallic oxide must be added.

5. The potassium permanganate must be added to complete oxidation.

6. It is entirely unnecessary to add metallic zinc to the contents of the distillation flasks, to prevent bumping, especially when a Fletcher's circular burner is at hand.

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*A figure enclosed in parenthesis refers to series.

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ON CERTAIN POINTS IN THE ESTIMATION OF BARIUM AS THE SULPHATE.*

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[Contributions from the Kent Chemical Laboratory of Yale College.]

In the received mode of precipitating barium as barium sulphate, three conditions are carefully observed—absence of excess of acid, slow mixing of the reagents and rest, before filtration, of twelve hours or until the precipitate has completely subsided. Usually, in this process, the precipitate is thrown out in a finely divided, milky condition and settles very slowly. My observation that the precipitate, under certain circumstances, is formed in a

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more crystalline condition and settles rapidly led me to investigate the conditions of so rapid a precipitation. These quickly settling precipitates were noticed, in the first instance, in the action of sulphuric acid upon solutions containing a very large amount of potassium chloride with hydrochloric acid in excess. In the course of five or ten minutes the precipitate had completely settled and was found to be in a distinctly crystalline condition and much coarser than the usual form of precipitated barium sulphate.

At the time, it was thought that the cause of this rapid subsidence was the alkaline salt present, and, accordingly, a series of experiments was made in which potassium, sodium and ammonium hydroxides were added in varying amounts to about 400 cc. of water, hydrochloric acid added to more than acidity (but not in measured amount), 0.5 gm. of barium chloride introduced, and precipitation brought about by adding dilute sulphuric acid. Sometimes these precipitates settled rapidly, but as often came down in the familiar milky condition. Later, another series of experiments, in which the different conditions were more carefully regulated, was made thus: in 400 cc. of water were dissolved 0.5 gm. of barium chloride, 10 cc. of strong hydrochloric acid, and amounts of the alkaline chlorides varying from 5 gms. to 0.05 gms., the whole being precipitated with 10 cc. of a solution of sulphuric acid made by diluting the concentrated acid with three parts of water. These precipitates all settled rapidly, and the variation in the amounts of alkali seemed to exert no very marked influence. Finally, these experiments seeming to point to hydrochloric acid as the influential factor, a series of experiments was made to test the effect of varying the amount of this acid. From a solution containing in 400 cc. 0.5 gm. of barium chloride and amounts of hydrochloric acid varying from 1 cc. to 50 cc., the barium was thrown out by means of 10 cc. of dilute sulphuric acid. This series showed that the hydrochloric acid had a very marked effect upon the precipitation of the barium sulphate. When only one or two cubic centimeters of hydrochloric acid were present, the precipitate appeared immediately, in a milky condition, and settled slowly as the amount of acid was increased, a point was soon reached where the precipitate was not so quickly apparent, but settled out

much more quickly and in a coarser condition. With 10 cc. to 15 cc. of strong hydrochloric acid in the solution, the precipitate settled clear in ten or twelve minutes and was in excellent condition for filtration. When the solution contained 50 cc. of acid, the precipitate settled clear in five minutes. Upon adding the sulphuric acid to such very acid solutions, no precipitate shows for a moment, but then it separates in beautiful crystalline condition and falls almost immediately. It can be safely filtered with or without pressure in ten minutes. In one instance, in the course of the experiments just detailed, 2 gms. of barium chloride were precipitated in the presence of 30 cc. of hydrochloric acid, the precipitate was allowed to settle clear, and was then filtered and washed, the whole operation being completed in seven minutes. This rapid subsidence of the precipitate is seen in hot solutions only—75° C. being the lowest temperature compatible with the attainment of good results, and 85° to 90° better.

To ascertain whether small amounts of barium would be precipitated in like manner from these acid solutions, a series of experiments was made with solutions containing in 400 cc., 10 cc. of hydrochloric acid and 5, 10, 15, 20, 25, 30 and 50 milligrams of barium chloride, precipitation being brought about as in the experiment above. These solutions remained clear a few minutes and then a very transparent precipitate appeared, but in no case was it as pronounced as the more finely divided precipitate produced in a neutral solution containing 5 mg. of barium chloride by the same amount of sulphuric acid. However, by giving a circular motion to the solution in the beaker, after about 20 minutes a small conical heap of barium sulphate was collected in each case in the centre of the beaker.

Experiments were next undertaken to ascertain whether barium is completely thrown out of solution when precipitated under the conditions related above. The barium salt used in all the experiments described below, was obtained by finely powdering selected crystals of barium chloride and drying by pressure between blotting papers. Portions of the same sample were used throughout. The hydrochloric acid used was the chemically pure article of commerce and had a specific gravity of 1.20. The sulphuric acid

used was, obtained by diluting the pure concentrated acid with three parts of water and had a specific gravity of 1.28.

In the first series the barium salt was dissolved in about 400 cc. of water, 15 cc. of hydrochloric were added, and precipitation was brought about by adding 10 cc. of the dilute sulphuric acid. The precipitates were filtered, after standing about ten minutes, upon asbestos felts in perforated platinum crucibles.

BaCl ₂ .2H ₂ O taken.	BaSO ₄ found.	Error.
(1) 0.5002 gm.	0.4760 gm.	0.0016 gm.—
(2) 0.5042 "	0.4812 "	0.0006 " —
(3) 0.5038 "	0.4786 "	0.0025 " —
(4) 0.5002 "	0.4760 "	0.0016 " —
(5) 0.5046 "	0.4812 "	0.0006 " —
(6) 0.5038 "	0.4804 "	0.0006 " —

The result of these determinations indicate plainly a loss of barium sulphate, but inasmuch as the felts used had been made very thin and it had been subsequently observed that a small quantity of the sulphate could be collected in one of the filtrates of the series by giving a circular motion to the water, it was thought that the thinness of the felts might offer an explanation of the loss and of the varying results of the series. The following series was, therefore, made in exactly the same manner except that care was taken to have the felts carefully made and reasonably thick.

BaCl ₂ .2H ₂ O taken.	BaSO ₄ found.	Error.
(7) 0.5014 gm.	0.4785 gm.	0.0004 gm.—
(8) 0.2227 "	0.2122 "	0.0005 " —
(9) 0.5003 "	0.4773 "	0.0004 " —
(10) 0.5046 "	0.4814 "	0.0004 " —

These results are uniform and indicate a trifling loss only; though in the filtrates of these experiments, also, a very slight, but, as it proved upon refiltering, unweighable amount of the sulphate could be collected. The precipitate in the last of these experiments was filtered off almost immediately after precipitation, and before it had completely subsided. In another case the whole operation, including the three weighings necessary was conducted to a finish in forty-five minutes.

In spite of the appearance of the trifling deposit in the filtrate, the deficiency in barium sulphate in these determinations was not greater than should be expected from the accepted solubility of

that salt in water. To ascertain the effect of strongly acid solutions upon the solubility of barium sulphate the following determinations were made.

In experiment (11) the same amounts of the sulphuric and hydrochloric acids, 10 cc. and 15 cc. respectively, were used as before, but the total volume was reduced to 100 cc. In (12) and (13) the same total volume as before, 400 cc. was used, but this volume contained 150 cc. of the strong hydrochloric acid instead of 15 cc. as in the preceding experiments.

BaCl ₂ ·2H ₂ O taken.	BaSO ₄ found.	Error.
(11) 0.5016 gm.	0.4888 gm.	0.0002 gm.—
(12) 0.5004 "	0.4779 "	0.0000 "
(13) 0.5001 "	0.4776 "	0.0000 "

It appears from these experiments that, as in the preceding series, the solubility of barium sulphate in solutions constituted as described is not increased by the free hydrochloric acid, and that the effect upon the solubility when this acid is present in great strength is to make the precipitate rather more insoluble, if anything, than it is in water. In this connection, it should be remarked that experiments of Fresenius,* together with somewhat similar experience gained by the writer in another line of work not included in this account, point to the fact that the presence of an excess of hydrochloric acid is an important condition of this high degree of insolubility. The exact amount of such excess has not been determined, but the amount used in the foregoing experiments seems to be sufficient.

In the preceding experiments, barium chloride was used in considerable quantity. The following determinations were made to ascertain whether very much smaller quantities of barium would come down as completely and as soon, or whether it is necessary to let the precipitations stand longer before filtration. In these experiments the barium salt was measured from a standard solution, containing 200 mg. of the chloride to the liter. The amounts of hydrochloric and sulphuric acids, 15 cc. and 10 cc. respectively, and the whole volume of the solution was the same as in the former experiments.

*Zeitschrift für anal. Chem., vol. ix, p. 62.

	BaCl ₂ .2H ₂ O taken.	BaSO ₄ found	Time in minutes between precipi- tation and filtra- tion.	Error.
(14)	0.0030 gm.	0.0024 gm.	120	0.0004 gm.—
(15)	0.0050 "	0.0046 "	150	0.0002 " —
(16)	0.0050 "	{ 0.0023 "	5	0.0025 " —
		{ 0.0043 "	60	0.0005 " —
(17)	0.0050 "	0.0031 "	5	0.0016 " —
(18)	0.0050 "	0.0040 "	10	0.0007 " —
(19)	0.0100 "	0.0078 "	10	0.0017 " —
(20)	0.0100 "	0.0085 "	15	0.0010 " —
(21)	0.0100 "	0.0083 "	30	0.0012 " —
(22)	0.0100 "	0.0087 "	60	0.0007 " —

From these results it would appear that the precipitation, in the presence of hydrochloric acid to the amount indicated, does not take place so rapidly when the amount of the barium salt is small but that two or three hours are sufficient for reasonably complete separation of the precipitate in any case.

In all the experiments described above there was no attempt at a gradual admixture of the reagents but they were measured out and at once added to the solutions, the whole being well stirred. From the results obtained, it appears to be established, as regards the usual precautions in precipitating barium by means of sulphuric acid, that, contrary to former usage, it is highly advantageous to have the solution strongly acid with hydrochloric acid; that it is not necessary to add the reagents drop by drop, but that the whole quantity required to complete the reaction may be added at once; that ordinary quantities of barium salts, in presence of a considerable excess of sulphuric and hydrochloric acids, are precipitated completely and at once, but that when only a few mg. are present, the precipitate requires more time to separate under the same conditions. Two or three hours are, however sufficient, and in no case is the excessive time of twelve hours required.

In the light of the fact demonstrated in the preceding account, that hydrochloric acid may be introduced freely, and without detriment to the quantitative exactness of the precipitation of barium in the form of sulphate from pure solutions, it seemed desirable to look somewhat into the question as to what the influence of a large excess of hydrochloric acid might be upon the well known contaminating effect of alkaline salts present during precipitation,

especially as it is customary to attempt the purification, of barium sulphate thrown down in the reverse of this process—the determination of sulphuric acid by means of a soluble barium salt—by digestion of the washed precipitate in hydrochloric acid. The following series of experiments was undertaken with this end in view. The details are shown in the tabular statement, precipitation being effected in the presence of free acid and the alkaline salt.

	BaCl ₂ ·2H ₂ O taken.	BaSO ₄ found.	Error.	HCl in Solution.	Alkaline Salts present.
(23)	0.5092 gm.	0.5032 gm.	0.0169 gm.	+ 110 cc.	KClO ₃ 3 gm.
(24)	0.5027 "	0.4907 "	0.0107 "	+ 10 "	" "
(25)	0.5026 "	0.4944 "	0.0154 "	+ 100 "	KCl 5 gm.
(26)	0.5045 "	0.4939 "	0.0122 "	+ 10 "	" "
(27)	0.5020 "	0.4931 "	0.0137 "	+ 10 "	" "
(28)	0.5013 "	0.4849 "	0.0061 "	+ 10 "	NaCl "

From the results it is plain that, whatever may be the effect of digesting the washed precipitate in hydrochloric acid, the presence of this acid in large excess during precipitation in the presence of alkaline salts, does not prevent contamination of the precipitate. On the contrary, the greatest contamination seems to have occurred in those cases in which the acid was present to the largest degree, but, in view of the slight variation in contamination as compared with the great differences in the amount of acid employed, it does not appear probable that the increase of acid has very much to do with the amount of contamination.

It likewise seemed to be a matter of some interest in this connection, to investigate the process by which it is currently supposed* that barium sulphate carrying alkaline salts may be effectually purified, viz: by the solution of the washed precipitate in strong sulphuric acid and reprecipitation by water. Accordingly the determinations of the following series were undertaken. The barium sulphate, precipitated from solutions containing 5 gms. of potassium chloride and 10 cc. of hydrochloric acid, was collected upon a filter, either paper or asbestos, and, after burning the paper or removing the precipitate from the asbestos (by tapping the crucible which held it and brushing out with a camel's hair brush),

*Fres. Quant. Anal., Vol. I, p. 547.

was dissolved by warming with concentrated sulphuric acid in a large porcelain crucible and, after cooling poured into water containing 15 cc. to 20 cc. of hydrochloric acid. The water into which the solutions in strong acid was poured was warmed with a view to diminish the milkiness of the precipitate, but care must be taken to keep the temperature below 60° C. to avoid danger of spattering on the addition of the sulphuric acid. In the last two of the experiments recorded a large amount of ammonium chloride was added to the water into which the solutions in acid were poured, but this appears to have been without influence upon the purification or the character of the precipitation. The precipitates, after settling clear, were filtered upon asbestos, ignited and weighed, the original felts being employed in those cases in which asbestos was used in the first instance. Those marked with an asterisk were gathered in the first filtration upon paper, the paper being burned in the crucible in which solution of the precipitate was subsequently effected. The remainder were filtered originally upon asbestos.

BaCl ₂ .2H ₂ O taken.	BaSO ₄ found.	Error.
(29) 0.5026 gm.	0.4746 gm.	0.0044 gm.—
(30) 0.5035 " *	0.4830 "	0.0022 " +
(31) 0.5016 "	0.4767 "	0.0024 " —
(32) 0.5025 "	0.4804 "	0.0050 " +
(33) 0.5046 " *	0.4829 "	0.0010 " +
(34) 0.5004 "	0.4825 "	0.0047 " +

These results show, evidently, that this process of purification is not satisfactory. It is possible that the losses observed may have been mechanical, and due to the violent action of the strong acid upon the water, but the excess in weight which is noticed in the majority of the determinations can only be attributed to residual contamination.

Certain experiments, on the other hand, in which the solvent action of sulphuric acid upon barium sulphate is utilized in a different manner resulted more favorably. When a solution of barium sulphate in sulphuric acid is evaporated to dryness, the salt, as is well known, is deposited in large crystals, which can be filtered off as readily as sand. The following series of experiments show the result of an attempt to utilize this property of comparatively slow and large crystallization in purifying the precipitate.

Solution of the precipitate was effected as in the experiments described above, and the evaporation of the acid was effected over a matting of asbestos, or by means of a ring burner, in porcelain, which is preferable to platinum when the evaporation is carried on as slowly as is necessary. After the acid was completely evaporated, the crystals were washed upon a felt of asbestos, ignited and weighed. Five gms. of potassium chloride and 10 cc. of hydrochloric acid were added to the solution of barium chloride in each case.

BaCl ₂ .2H ₂ O taken.	BaSO ₄ found.	Error.
(35) 0.5029 gm.	0.4796 gm.	0.0006 gm.—
(36) 0.5008 "	0.4783 "	0.0001 " +
(37) 0.5038 "	0.4810 "	0.0001 " —
(38) 0.5087 "	0.4861 "	0.0003 " +
(39) 0.5025 "	0.4795 "	0.0006 " +

These results are plainly good and satisfactory so far as concerns the purification of the salt, but, when the evaporation is conducted in the manner described, several hours are needed for the evaporation, and great care must be exercised to obviate the danger of snapping which becomes manifest in the later stage of the evaporation.

By the aid, however, of a Hempel evaporating burner* the operation can be finished safely, and with but little care, in the course of half an hour. The following determinations were made exactly like those of the last series, with the exception that the evaporation was effected by means of the Hempel apparatus.

BaCl ₂ .2H ₂ O taken.	BaSO ₄ found.	Error.
(40) 0.5050 gm.	0.4824 gm.	0.0002 gm. +
(41) 0.5069 "	0.4838 "	0.0000 " —
(42) 0.5041 "	0.4825 "	0.0021 " +
(43) 0.5021 "	0.4812 "	0.0018 " +
(44) 0.4033 "	0.4801 "	0.0005 " —

Though not an absolutely perfect process, the purification of barium sulphate by this method of solution and evaporation is evidently better, by far, than the old method of solution and reprecipitation by dilution.

The writer gratefully acknowledges his indebtedness to Prof. F. A. Goöch for many helpful criticisms and suggestions during the course of this investigation.

*Ber. d. deutsch. chem. Ges., xxi, p. 900. See also this Journal, April, 1891, p. 181, and Vol. III, p. 121.

ON THE IODINE NUMBER FOR LARD OIL BY THE HÜBL METHOD.

BY REUBEN HAINES.

Several years ago the writer made a large number of examinations of various oils and fats by the Hübl method, including among them lard oil. Although several determinations of the "Iodine Number" for lard oil have been published, the writer thinks it worth while to put upon record the results which he had obtained.

Three samples of lard were first obtained, two of them directly from two lard factories put up ready for the market and expressly stated to be pure articles; and the third sample from a farmer who was accustomed to serve the writer's family with lard. These lards were tested for purity by tests in use at that time and all were passed as genuine and unadulterated. The two factory lards had a melting point of 45° C., while the country lard was much softer and had a much lower melting point (33° C. was found, but this was possibly 2° or 3° too low). The Iodine Numbers found for these samples of lard were as follows:

Factory lard No. 1 (average of 3 tests)	62.30
" " No. 2 " " 4 "	62.49
Country lard " " 2 "	59.33

The oil was then pressed out of each sample separately in the laboratory by means of an ordinary hand drug press, the temperature of the room being regulated to an average slightly below 50° Fahr., never exceeding 55° nor going below 45°, the time of year being favorable for that object.

The pressure of the screw was gradually increased to the utmost that the press was capable of producing.

The oils obtained from these lards did not chill or become turbid until about 45° Fahr. The temperature maintained in the pressing and the "cold test" of the oil produced are identical with factory practice. On being submitted to the Hübl test these oils gave the following results for the Iodine Number:

Oil from Factory lard No. 1 (average of 5 tests)	75.14
" " " 2 " "	73.03
" Country lard " "	70.01
Average for oil from both factory lards	74.01
" " the three oils	72.72

These oils contained Free Fatty Acid equivalent to Oleic Acid 0.86 per cent., 0.49 per cent., and 1.35 per cent. respectively, a short time after the above Iodine Numbers were obtained.

A peculiarity noticeable which I am unable to explain is the fact that the country lard of low melting point and also the lard oil made from it have lower Iodine Numbers than the other lards and the oils from them. Nevertheless the tests were all made with equal care to avoid error.

The same two oils made from factory lards were recently tested by the modified Bechi test (omitting the rapeseed oil and amyl alcohol and acidifying only very slightly with nitric acid), but no darkening of color was produced after heating exactly 15 minutes on a water-bath. The sample of oil from country lard was lost and was not tested in this manner. There had been but slight increase in acidity in the oils from factory lards.

A sample of Prime Lard Oil was obtained from a reputable dealer who guaranteed it to be strictly pure from their knowledge of the manufacturers of it. This oil was obtained at about the same time as the above mentioned samples of lard. On being tested by the Hübl method the Iodine Number was found to be 74.02 as the average of four consecutive tests. It was also examined recently by the above modified Bechi test, and it did not become darkened in color. The rise of temperature by Maumene's test was found to be 42° C., the experiment being made in the manner recommended by Allen.

Recently also the Iodine Numbers for the oil made from factory lard No. 1 (same sample as tested before) and for the above mentioned sample of Prime lard oil were redetermined with very great care in regard to the details of manipulation. The following results were obtained :

Oil from Factory lard No. 1—two consecutive tests	72.34 ; 72.33
Prime lard oil—single test	73.73

The difference from the former figures may have been largely owing to the fact that in these later tests greater care was taken to secure perfect uniformity of temperature during the experiments and to have a large excess of iodine in the titration, about equal to the quantity absorbed by the oil. In the former experiments the titrations were made at the expiration of two to three hours ;

in the latter ones the time was extended to six hours. Three hours is, however, found to be sufficient for non-drying oils. In the last experiments a burette with a glass stopper at the top and a small hole for admission of air was used for the Iodine Solution instead of closing an ordinary burette with a cork as was done previously. A delicate thermometer was kept constantly almost in contact with the burette. Equal measured quantities of potassium iodide solution and of chloroform in the tests and blank experiments, and only the purest chloroform was used; in the last experiments chloroform of the grade used for inhalation in medical practice.

PHILADELPHIA, PA.

LOCAL STANDARDS IN WATER ANALYSIS.

BY REUBEN HAINES, PHILADELPHIA, PA.

In the analysis of potable water it is desirable to have, whenever possible, "Local Standards" established for different sections of country or districts, and for separate classes of waters, since it is difficult, or even impossible, to find any single standard of general character that will be applicable to all conditions for the purpose of passing judgment on a given water as regards wholesomeness for drinking. (Vide Reports and Papers by Mallet, Nichols, Dupre & Hehner, Leeds, et al.)

Local standards for well waters can be obtained by analyses of a number of such well and spring waters of a given district as are in a natural uncontaminated condition. These form standards of *purity* to which a potable water should conform pretty closely. In addition to these, a limit should be ascertained for each locality which might be called "highest limit," beyond which no water of that district and of that particular class should go if it is to be considered wholesome, except under certain conditions.

Dr. A. R. Leeds has said in regard to this subject in his Report to the City of Wilmington, Del., 1882, On the Water Supply of that City: "The best of these standards of purity are those which long-continued observation and analysis show to be true of the particular river or true of the particular class of wells in a certain restricted locality. It will not answer to apply to wells located at Ocean Grove the same standards as to those located in New York City; nor to either, the same standards as those which are applicable to a river contaminated by sewage and factory refuse

like the Passaic or the Brandywine. The water analyst, by constant comparison of his analyses with the sanitary properties of the waters analyzed, becomes able to set up a standard from which the water does not depart without becoming more and more objectionable."

It is however true that one cannot well apply such standards as "hard and fast rules." As the modes by which pollution may occur, and the character of the contaminating material are numberless, so also the degree to which such pollution may be dangerous will vary with the special conditions. The present writer fully coincides with the statement made by the late Prof. Wm. Ripley Nichols that "there always will be difficulty in deciding how near to any limit any suspicious water may come and still be used with a reasonable degree of safety," and that "every doubtful water must be considered by itself with all the light that can be brought to bear upon it."*

This, however, does not necessarily exclude the idea that a standard would be practicable or be an aid to the judgment, if a certain amount of latitude is provided for to satisfy special conditions.

Strictly speaking, a pure drinking water should be one which is altogether above suspicion of *any* contamination with sewage or other injurious substances. This, however, may not be practically obtainable in a given locality, and the question then occurs, what constitutes a reasonably pure water under the special circumstances, and to what extent may evidence of slight contamination be disregarded without imperilling the health, whether at the present time or in the near future; for we must look beyond the present conditions, since where there is a small amount of contamination in a well at the present time, the soil may soon become clogged, efficient filtration cease, and organized substance pass into the water through some channel suddenly formed, it may be, by a heavy rainfall.

The range, then, between the "standard for purity" and the "highest limit," as proposed for a given locality, would afford sufficient scope for judgment after inspection of the premises and obtaining other information connected with the well.

Considered generally, it may be stated that the limit given by Wanklyn for Free and Albuminoid Ammonia, namely:—Free NH_3 ,

*Water Supply, Chemical and Sanitary. Wm. Ripley Nichols, 1883, pp. 40 and 41.

not over 0.005 parts in 100,000; Albuminoid NH_3 0.010 parts to be considered suspicious, and 0.015 parts and over to be condemned absolutely;—may be regarded as judicious, especially as stated by Dr. Smart “in the case of well waters in the denser settlements; and in every case when an animal origin to the organic matter is indicated by careful survey or chemical analysis.* W. R. Nichols† practically indorsed this opinion, holding that a good well water should not contain over 0.010 part albuminoid NH_3 . Some other chemists have either advocated or adopted a higher limit. C. R. Stuntz‡ adopted the scale .010 to .015 parts = good water; .020 to .025 parts = bad water. Tiemann and Gärtner§ prefer the limit 0.020 parts for albuminoid NH_3 , and state their reasons for not adopting the lower standard used by other chemists.

In cases, however, where only vegetable contamination of *natural* origin is possible, a larger amount of albuminoid NH_3 should be considered permissible than in the case of *animal* pollution.

In regard to chlorine, evidently no fixed rule is applicable to all places. Shallow wells in the sand near the sea certainly may be expected to contain considerable chlorine, while these will be apt to vary among themselves. Deep wells sunk into certain geological strata may yield waters containing comparatively large amounts of chlorine, although organically pure and otherwise suitable for drinking.

Generally, however, in shallow well waters the chlorine should not much exceed 1.0 part in 100,000. Prof. W. R. Nichols stated this figure as a limit for Massachusetts. Hard waters containing sulphates have been frequently found by the writer to contain rather more chlorine than soft waters, and for this class he prefers the limit of 2.0 parts in 100,000 for vicinity of Philadelphia. Tiemann and Gärtner|| state the limit as 2.0 to 3.0 parts. Dr. E. Frankland¶ states that if the water contains less than 1.0 part, it is probably free from contamination by sewage, but if more than 5.0 parts, the condemnation of the water is rarely unmerited. Other

*Water Supply, Sanitary and Chemical, by W. R. Nichols, page 131, quoted by Prof. Nichols.

†Idem, p. 131.

‡Report of Analyses of Ohio River Water by Order of Board of Health of Cincinnati, 1881, by C. R. Stuntz, M. D.

§Die Chemische und Microscopisch-bakteriologische Untersuchung des Wassers (1889) page 651.

||Op. cit., p. 651.

¶Water Analysis, p. 28.

authorities give limits varying from 0.8 parts to 3.5 parts per 100,000.*

Wells at the sea-side may vary in chlorine according to the influence of salt spray driven inland by winds. Wells in sheltered situations at the sea-side may contain very little more chlorine than those located many miles inland. At Newport, the writer found a very good well stated to have good surroundings, located in the outlying parts of the old town on the Bay side, which contained 1.9 parts chlorine in 100,000; while an uncontaminated well at Easton's Point on the opposite side of the island and exposed to the direct influence of the sea, contained 3.2 parts in 100,000. Easton's Pond (a fresh water pond used for the public water supply of Newport) not far distant, contained at that time (1883) 4.6 parts in 100,000, and Prof. Mallet† had found a couple of years previously in this same pond water 2.25 parts in 100,000. The writer however also found in 1883, at Cape May Point, in a well close to the shore and with suspicious surroundings, only 3.2 parts, while the public water supply of Cape May City at the same time contained 3.85 parts per 100,000.

As regards nitrates, it is conceded by most chemists that presence of this salt in considerable amount is a very suspicious circumstance.

Prof. Mallet is inclined to place great importance on the estimation of nitrates and nitrites, because in general showing a much clearer distinction between good and bad natural water than the results from the estimation of organic matter by the several processes generally used.‡ Widely varying limits, however, have been proposed for the amount of nitric acid allowable for a good water, while for nitrites entire absence or only minute trace is considered proper. The writer's own experience leads him to adopt, provisionally, the limit of 1.0 parts nitrogen as nitrates in 100,000, which a good water should not much exceed, while the great majority of uncontaminated well waters contain less than half of that amount.

The utility of such local standards, if established satisfactorily, is acknowledged by Tiemann and Gärtner§: for these authors say

*Analyst, Vol. 14, p. 205.

†Report of Nat. Board of Health, 1882.

‡Report of the Nat. Board of Health, 1882, p. 201.

§Op. Cit., p. 652. See also Dupre & Hehner and Ashby & Hehner, Analyst, Vol. 8, pp. 53-62.

that useful local standards may be founded upon the average composition of a series of waters in different places in a given district which are well known to be completely protected from pollution; and that such standards are even decidedly preferable to the general standard which they themselves have given.

They seem to doubt, however, the feasibility of obtaining such local standards for the following reasons stated by them: 1st, That the soil and rock of extensive tracts of land are seldom sufficiently similar. 2nd, That reliable local standards could be established only in an isolated manner. 3rd, That the analyst is seldom in a position to apply himself to that special purpose.

It would seem, however, that these objections are by no means prohibitory. The variations occurring through differences in geological character of a district may be readily ascertained as regards shallow wells at least, in the course of collecting the various samples for analysis, and an approximate allowance may be made for the influence of these geological or mineralogical differences. Indeed, in reporting upon even a single well, some authorities state that the chemist should always ascertain and make due allowance for the special geological features of the district in which the well is situated. Prof. W. R. Nichols said,* "the chemist should know as much as possible as to the history and source of the water and if possible take the sample himself—that is, if he is to express an opinion as to the suitableness of the water for drinking." He fully endorsed the recommendations of Dr. Fox† on this point, viz: "It is a golden rule in water analysis never to give an opinion unless the analyst knows (1) the nature of the source of the water, whether it comes from a spring or well or river or rain reservoir, etc.; (2) the depth of the well if it is withdrawn from one; (3) the geology of the district from which it is derived, together with the character of the soil and subsoil; (4) the distance from the source of the water of the nearest filth or drain."

It is true that often the individual chemist may not have the opportunity to investigate for himself a large number of waters of a particular district for the purpose of setting up a standard for comparison. Yet if several chemists were mutually to contribute such results obtained in that district as they may be permitted to do, it would not probably be long before a satisfactory local standard could be established.

*Op. Cit., p. 44.

†Sanitary Examination of Water, Air and Food, London, 1878.

The writer has, therefore, ventured to contribute in the following tabular statement the results of a number of analyses he has made during the past fourteen years of well waters in the vicinity of Philadelphia, in rural and suburban districts, which he believes, both from analysis and from personal inspection of the premises, to be entirely uncontaminated by sewage. They are wholly confined to the west side of the Delaware river.

It may be stated that other estimations were in many instances made in addition to those given, as for example the oxygen required by the permanganate test. As, however, part of the time, Tidy's method and later the Kubel form of the method were used, their results being different, both are omitted from the following statement.

In the column of "nitrogen in nitrates" an asterisk (*) denotes that a qualitative test by FeSO_4 solution in 5 or 10 cc. of the sample of water without concentration gave no reaction or only the faintest possible color after standing $\frac{1}{2}$ hour in cold water and protected from strong light. In this test blanks were made to prove the purity of the H_2SO_4 used. With care it could be made to show about 1.0 part of nitrogen as nitrates in 100,000 of water without concentration. The quantitative estimations of nitrogen as nitrates were made either by Williams copper-zinc couple method or by the phenol-sulphonic acid method.

All numerical results are stated in parts in 100,000.

Germantown.

No.	Description, Location, &c.		Date.	Free NH_3 .	Alb. NH_3 .	Cl.	Nitro- gen in N_2O_5 .	Total Solids.
1	Haines St., E. of Chew	Well	1877	.0014	.0034	1.00
2	" "	"	1883	.0040	.0040	.80	*	...
3	" "	"	1886	None	.0036	1.80	.247	11.0
4	" "	Spring	1877	.0012	.0030
5	" "	"	1884	.0012	.0034	1.00	*	...
6	" "	"	1889	.0010	.0052	.80	...	10.5
7	" "	"	1889	None	.0030	.80	*	...
8	High St.	Well	1877	.0026	.0064	1.40	*	5.0
9	Mill St., E. of Willow	"	1880	.0022	.0062	1.80	*	22.8
10	Clapier St.	Spring	1889	.0010	.0052	1.60	.720	13.0
11	West Chelton Ave. .	Well	1877	.0040	.0052	1.00	*	8.5
12	Wayne Junction . .	"	1882	.0026	.0050	1.80	.520	...
	Average0018	.0045	1.15	.495	11.8

Nos. 1 to 9 are situated on the east side of Germantown avenue, the main street of the town. Nos. 10 to 12 are situated on the west side of the town. No. 9 is slightly hard from sulphates. The rest are soft waters. Nos. 9 and 11 are in the central part of the town. Nos. 4, 5, 6 and 7 are analyses of the same spring.

Frankford—Branchtown—Chelton Hills.

No.	Description, Location, &c.		Date.	Free NH ₃ .	Alb. NH ₃ .	Cl.	Nitro- gen in N ₂ O ₅ .	Total Solids.
13	Vicinity of Frankford	Well	1886	.0040	.0030	1.10	.741	10.5
14	In Woods near "	Spring	1888	None	.0030	.80	.257	9.0
15	York Road.	Well	1890	None	.0040	1.20	.150	10.0
16	"	"	1881	.0010	.0040	2.00	*	7.5
17	Washington Lane	"	1886	.0010	.0050	1.00	.412	10.5
18	"	"	1889	None	.0050	.80	.370	9.0
Average0010	.0040	1.15	.322	9.4

Haverford and Bryn Mawr.

No.	Description, Location, &c.		Date.	Free NH ₃ .	Alb. NH ₃ .	Cl.	Nitro- gen in N ₂ O ₅ .	Total Solids.
19	Vicinity of Hav. Col.	Well	1880	.0010	.0056	1.10	*	12.9
20	"	"	1889	.0048	.0046	.70	.600	9.0
21	"	Spring	1891	.0020	.0070	1.00	.750	11.5
22	Bryn Mawr	"	1880	.0022	.0070	.70	*	5.7
23	"	"	1881	.0010	.0030	.70	*	5.0
24	"	"	1883	.0026	.0066	.60	.263	4.5
25	"	Well	1880	.0040	.0050	1.10	*	10.0
26	"	"	1883	.0010	.0038	1.20	.347	8.5
27	"	"	1888	.0026	.0030	.70	.412	7.4
Average0023	.0051	.87	.474	8.3

Overbrook.

No.	Description, Location, &c.		Date.	Free NH ₃ .	Alb. NH ₃ .	Cl.	Nitro- gen in N ₂ O ₅ .	Total Solids.
28	E. of Pa. R.R. Station	Well	1882	.0046	.0040	1.45	*	12.0
29	W. " " "	Spring	1887	.0040	.0030	.70	.249	10.5
Average0043	.0035	1.07	.249	11.2

Spring Mill below Conshohocken.

No.	Description, Location, &c.		Date.	Free NH ₃ .	Alb. NH ₃ .	Cl.	Nitrogen in N ₂ O ₅ .	Total Solids.
30	Large Public Spring. Lime-stone Water Hardness.	12.2°	1889	.0040	.0050	.50	.370	16.5

Deep Bored or "Artesian" Well.

No.	Description, Location, &c.	Date.	Free NH ₃ .	Alb. NH ₃ .	Cl.	Nitrogen in N ₂ O ₅ .	Total Solids.
31	Germantown—312 feet deep	1877	.0020	.0040	3.00	*	30.0
32	Columbia Ave., near Broad St.	1886	.0160	.0030	1.50	.135	28.0
33	Vicinity of Darby, Del. Co., Pa.	1889	.0010	.0050	1.10	.470	. . .
34	N. Penna. R. R., near Phila.	1890	.0044	.0030	1.10	.100	15.0

Nos. 17 and 18 are analyses of the same well and Nos. 22, 23 and 24 of the same spring respectively.

In regard to the above "artesian" wells, it may be said that No. 31 was sunk in 1875. The rock was struck at 8 feet from the surface, and is said to have been of a soft schistose character throughout the whole depth, about midway very garnetiferous. A six inch iron tube extends the whole depth. The water rises to a level of 13 feet below the surface and the supply is about 40 gallons per minute. Since the above analysis was made, the water has increased in total solids and in hardness, and has become impure. It is now seldom used.

Wells No. 32, 33 and 34 are from 100 to 125 feet in depth and recently sunk.

These deep wells have not been included in the averages for shallow well water, as they may be considered to belong to a somewhat different class.

The total averages for the shallow wells above given, calculated only from the *numerical* results found, are as follows:

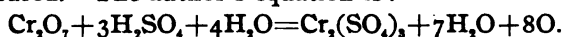
Free NH ₃ .	Album. NH ₃ .	Chlorine.	Nitrogen in Nitrates.	Total Solids.
.0020	.0045	1.07	.427	9.6

These figures I propose as a standard for pure water in the district as designated. The nitrates, however, being quantitatively determined in only about one-half of the analyses, renders the average in that respect less conclusive than the other parts of the series.

NEW METHODS IN QUANTITATIVE ANALYSIS.

The fact that a blue color is produced and a certain amount of oxygen liberated when chromic acid is treated with peroxide of hydrogen, is the basis of the methods proposed by the author.

1. *Estimation of Chromic Acid.*—Wagner's Azotometer, or Knop's together with the evolution glass, is used for these determinations. The liquid containing the chromic acid, which must not be too concentrated, being of about 10 to 15 cc. volume, is brought together with 10 cc. of dilute sulphuric acid (1:5) in the larger portion of the apparatus. 5 to 10 cc. of commercial peroxide of hydrogen is placed in the cylinder. After the apparatus has stood in water of the temperature of the room for ten to fifteen minutes, the levels in the U tube are the same, and the water in the mixing tube at zero, the peroxide is allowed to flow into the chromic acid solution until the blue color appears. After being well shaken, the apparatus is again placed in water for ten to fifteen minutes, when the levels are compared and the volume of gas measured. The author's equation is:



i. e., 1 gm. $\text{CrO}_3 = 0.6363$ gm. O,

or 445.3 cc. at 0° and 760 mm. pressure.

1 gm. $\text{K}_2\text{Cr}_2\text{O}_7 = 0.4333$ gm. or 3032 cc. O.

Hydrochloric acid may be used in place of sulphuric if the quantity of free acid is not more than 4 cc. of 1-2 acid to 40 cc. of the diluted chrome solution; more than this amount would liberate chlorine. Nitric acid may be present to the amount of 0.2. Acetic acid and succinic acid have no action, but tartaric acid, oxalic acid, sugar, alcohol, or any substance that is oxidized by chromic acid, will of course cause bad results. This method will give the amount of chromic acid, or the amount of "active" oxygen in a solution of bichromate of potassium, but the volume of gas liberated must be multiplied by $\frac{3}{8}$ or .375, as only three of the eight atoms of oxygen liberated from one molecule of bichromate are considered as "active."

2. *Estimation of Oxide of Chrome.*—When it is not too difficult to convert the oxide into chromic acid, this method can be used to advantage. The peroxide of hydrogen is best used in an alkaline solution, when, after oxidation, the excess of peroxide is driven off by boiling. The solution is then neutralized by sulphuric acid and the gas volume measured.

$$\begin{aligned} 1 \text{ cc. O} &= 1.710 \text{ CrO}_3. \\ 1 \text{ mg. O} &= 1.187 \text{ chromic oxide.} \end{aligned}$$

In examining chrome iron ore when decomposition is effected by fusion with nitre and carbonate of soda, it must be borne in mind that an excess of nitrates spoil the results.

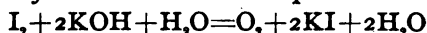
3. *Estimation of Sulphuric Acid.*—This indirect method depends upon the fact, shown by Mohr, that the sulphuric acid in a liquid may be replaced by an equivalent amount of chromic acid.

The solution is placed in a 100 cc. stoppered flask and precipitated, cold, with a solution of barium chromate in hydrochloric acid, thoroughly shaken, and allowed to stand for one-half hour, diluted to about 90 cc., ammonia added to alkaline reaction, filled to the mark, well shaken, and filtered on a ribbed filter. 25 to 60 cc., according to the amount of chromic acid, of the filtrate are placed in the evolution tube of the apparatus, 10 cc. of sulphuric acid added, and the chromic acid determined by peroxide of hydrogen in the usual way.

$$\begin{aligned} 1 \text{ cc. O} &= 1.787636 \text{ mg. SO}_3. \\ 1 \text{ mg. O} &= 1.2509 \text{ mg. SO}_3. \end{aligned}$$

Commercial "pure" chromate of barium contains potassium chromate and ammonium chromate, and must be purified before being used.

4. *Estimation of Free Iodine.*—The equation



will explain the grounds for this determination. In the larger portion of the apparatus is placed the solution containing the iodine, in iodide of potassium—about 40 to 50 cc. In the cylinder are placed 5 cc. of a 2% solution of peroxide of hydrogen and 10 cc. of potash solution (1 KOH—2 H₂O). After cooling to the temperature of the room, the liquids are mixed as in the former determinations, and the volume of gas measured. From the author's tables for gasometry, the corrections are made for temperature and pressure.

5. *Estimation of Combined Iodine and Iodic Acid.*—For the determination of the iodine in iodides the iodine is distilled with acid sulphate of iron and caught in iodide of potassium solution and treated as usual. For iodates, to the solution containing the iodate is added iodide of potassium and an excess of either sul-

phuric or hydrochloric acid, and the liberated iodine determined in the usual way.

6. *Acidimetry*.—1 to 2 gms. of finely pulverized iodate of potassium, dissolved in a little water, with about 10 gms. of iodide of potassium, are put into the apparatus and a convenient amount of the acid to be examined, which must be dilute, is allowed to flow into it. Iodine is at once liberated and absorbed by the excess of iodide of potassium. The solution is then diluted to about 40 cc., hydrogen peroxide and caustic potash solution are placed in the cylinder, and the volume of gas determined in the usual way. The volume found is referred to the tables for hydrogen and the weight of the acid found at once. This weight multiplied by the "equivalent weight" for the acid in question will give the percentage.

For the estimation of organic acids, a separate flask (stoppered) is used. The iodine is set free and absorbed again in iodide of potassium by standing this flask, with the liquids in it, for one-half hour, in water kept at 70°. After all action is completed, and the liquid is cooled, it is poured into the evolution apparatus and the process carried out as in the other instances.

The acidity of beer and the total acids in wine may also be determined by this method, and numerous examples show excellent results as compared with titration methods. (A. Boumann, *Ztschr. Angew. Chem.*, 1891, 135.) J. R. W.

NOTES.

Solubility Determinations.—J. B. Coleman recommends that for determinations of solubility at ordinary temperature, the coarsely powdered solid be suspended in the solvent and a current of air aspirated through. With KClO_4 , 15 minutes' aspiration was sufficient, and with CuSO_4 half an hour. The air is saturated with the vapor of water or of any other solvent to be used by first passing it through the liquid in a separate bottle. With oxidizable substances, coal gas freed from oxygen and carbon dioxide by alkaline pyrogallate is used.—(*J. Soc. Chem. Ind.* 10, 231.) E. H.

Standard Method of Sampling Iron Ores.—All samples shall be taken from the vessel while unloading, and no part of it shall be taken before "bottom is made." As soon as bottom is struck

under each hatch exposing faces of ore from top to bottom of the cargo, the sampler is to begin sampling as follows :

Starting at one side of a face of ore, he is to sample the whole of it at intervals of eighteen inches, the exact point being determined by a measuring rod. When the end of the rod falls upon lump ore, lump ore is to be taken into the sample at that point. When the end of the rod falls upon fine ore, then fine ore is to be taken into the sample, the same weight as nearly as possible shall be taken at each sampling point. All the faces shall be sampled in this manner ; this sampling shall be repeated at intervals of two hours, which would require not less than four samplings to be made of an ordinary cargo, and no less than three samplings shall be made of any cargo of over 500 tons.

The total weight of the sample shall in no case be less than 300 pounds, and the whole of it shall be ground fine enough to pass through a No. 3 sieve. After being put through this sieve, the samples shall be spread out, thoroughly mixed, and quartered repeatedly, rejecting alternate quarters each time until the sample is small enough for shipment to the laboratory, namely four or five pounds. Upon receiving this sample at the laboratory, it shall all be ground fine enough to pass through a No. 6 sieve, after which it shall be quartered again and the remaining portion so reduced as to pass through a No. 80 sieve, again quartered, and put through a No. 120 sieve ; this last powder shall be recognized as the sample of the cargo from which the ore was taken, and the analysis of this powder dried at 212 degrees Fahrenheit shall be accepted as the analysis of the cargo.

The analyst shall, in case it is so desired, send to either the buyer or seller a portion of the powdered sample from which the analysis has been made, and also a copy of said analysis.

Whenever the above method of sampling shall be made a part of any contract, it shall be understood that the buyer and seller shall divide equally the expenses of such sampling and analysis, *unless* it is otherwise specified.

Both buyer and seller shall have the right to have a representative present while samplings are being made, and if sampling is not carried out properly, to object at the time, but if no objection shall be made, the sampling shall be considered satisfactory. (From a pamphlet issued by Rattle & Nye, Cleveland, Ohio.)

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ON THE DETERMINATION OF NITRATES IN WATER.

BY ALLEN HAZEN AND HARRY W. CLARK.

I. PHENOLSULPHONIC ACID PROCESS.

The accurate determination of nitrates, in large numbers of samples of water, has presented considerable difficulty. A few years ago, the phenolsulphonic acid process,* was selected, as being, on the whole, the most satisfactory, and with it we have made several thousand determinations.

The process consists, essentially, of evaporating a measured portion of water to dryness, and treating the residue with a solution of phenol in sulphuric acid, a portion of which, the nitric acid liberated converts into nitrophenols, which when made alkaline, are strongly yellow. The color so produced is compared with that obtained in a similar way from known quantities of potassium nitrate.

The accuracy of the results was greatly increased by adding sodium carbonate to prevent the loss of nitric acid during evaporation, and by decolorizing yellow surface waters by alumina.

The best results were obtained with about 1 cc. of a 5 per cent. solution of strictly pure phenol in sulphuric acid nearly free from water, added to the dry residue, and without warming. Caustic soda or potash was substituted for ammonia, in neutralization, to avoid the fumes of the latter.

*Grandval and Lajoux. C. R., July 6, 1885.

An attempt was made to use standards made from pure picric acid, but, to our surprise, their color was only a third as deep as that of standards made by treating potassium nitrate with phenolsulphonic acid. Other nitrophenols were then tried, but none matched the standards perfectly. It was possible to match particular standards by mixing different nitro-compounds, but for other standards, different mixtures were required. It was obvious that in our standards, prepared from potassium nitrate, we were not dealing with a pure compound, but with a mixture of varying proportions of different nitrophenols, and as the different compounds are by no means of the same color for equal contents of nitrogen, variations in the proportions of the different compounds formed, gave rise to very serious errors. The principle products are usually ortho- and para-mononitrophenol in varying proportions.

The following table shows the strength of solutions of some of the nitrophenols which give colors equal to those of average standards prepared from potassium nitrate, when seen through a depth of eight inches of solution:

Comparison of Solutions of Nitrophenols.

(Parts per Million Nitrogen in a Depth of 8 Inches.

Standard from KNO_3 .	Orthomono- Nitrophenol.	Paramono- Nitrophenol.	Dinitro- phenol.	Trinitro phenol.
.02	.022	.014	.04	.06
.04	.040	.026	.08	.14
.06	.060	.044	.12	.22
.08	.076	.064	.18	.32
.10	.090	.08	.23	.42
.12	.110	.12	.31	.60
.14	.124	.16	.38	.80
.20	.16	.36	.60	1.40
.40	.22	1.80	1.40	3.00
.60	.30	7.00	3.00	6.00
1.00	.38	12.00	6.00	9.00
1.40	.46		9.00	
4.00	1.00			
10.00	2.00			

We have not been successful in so controlling the reaction as to

get a constant product, or in finding a substituted phenol with which there can be only a single nitro-compound, and which is, at the same time, sufficiently soluble in water, and otherwise adapted to the process. If such a compound could be found, the accuracy of the process might be greatly increased.

The presence of chlorine lowers the result, often seriously. The error increases with the ratio of chlorine to nitrate, but is not proportional to it. Numerous experiments do not show sufficient regularity to allow even an approximate estimate of the error in particular cases. The results of this process upon a hundred and fifty ground waters averaged 11 per cent. lower than the results obtained by reduction by the aluminum process, with the precautions to be described, and it is believed that this represents approximately the average error due to chlorine in these particular cases. In some instances we have removed the chlorine with silver sulphate, and obtained higher results; but even then the results are liable to the errors described above.

This process, with proper precautions, gives results usually too low, and often much too low, and while it may be useful in some cases, we have been unable to obtain results of the desired accuracy.

II. ALUMINUM PROCESS.

As usually described,* the aluminum process for the determination of nitrates consists of boiling a portion of the water with caustic soda, to expel ammonia, and after cooling, adding a piece of aluminum foil. The hydrogen evolved reduces the nitrates and nitrites present to ammonia. The hydrogen is taken through dilute acid to hold any ammonia that may be given off. After reduction is complete, the acid is washed into the water, and the ammonia distilled and nesslerized.

The process may be divided into two parts: the reduction to ammonia, and the estimation of the ammonia formed. For convenience, we shall first consider the determination of the ammonia, and afterward the conditions of complete reduction.

The amount of ammonia removed by the hydrogen is ordinarily

*Sutton Volumetric Analysis, Fifth Edition, p. 364.

so small that it seemed better to estimate its quantity, and apply a correction, rather than use the troublesome absorption tubes of glass moistened with acid. The proportion of ammonia removed depends upon temperature and the amount of aluminum dissolved. Fifty cubic centimeters of water saturated with ammonia at 20 degrees holds 26 gms. If the water contains .001 gm. of ammonia, it is $\frac{1}{26,000}$ saturated. One gram of aluminum in dissolving gives off 1200 cc. of hydrogen, and, supposing the ammonia to obey exactly the laws of gases, this should carry $\frac{1}{26,000}$ of its volume of ammonia, or 0.046 cc. weighing 0.000035 gm. or 3.5 per cent. of the whole amount of ammonia present. With different amounts of aluminum, and the same volume of water, the loss is directly proportional to it, being 1.75 per cent. when $\frac{1}{2}$ gm. is dissolved. With different amounts of ammonia, the same percentage is removed. At higher temperatures, the loss is greater, becoming 4.6 per cent. at 30 degrees for 1 gm. of aluminum in 50 cc. With reduced pressure, the loss is greater, and is inversely proportional to the pressure. The loss from a nitrate solution is slightly less than from an ammonia solution, because there is no ammonia to be lost when the first hydrogen is given off.

Numerous experiments, keeping the acid separate from the bulk of the water, show that the above estimates are slightly above the truth, but they form a satisfactory basis for corrections, which practically never exceed 2 per cent.

We have found that, with ground waters at least, distillation of the ammonia after reduction is unnecessary, quite as good results being obtained by diluting an aliquot portion, and nesslerizing direct. The conditions of success of this process are that the water after reduction shall be practically colorless, and free from the black residue of the aluminum, and that no alumina shall precipitate before nesslerization. The reducing action of the nascent hydrogen, with the caustic alkali and the carbonate always present, clarifies a majority of waters sufficiently, and it is only with yellow swamp waters with low nitrates, where large volumes must be taken for the determination, that the color interferes with the result. Waters usually settle so clear after the action that suspended matters are not troublesome. The separation

of alumina causes the greatest difficulty, clouding the tube, and often seriously lowering the readings. This can be prevented by using for dilution, distilled water entirely free from carbonic acid. Such water can be easily prepared by blowing steam through ordinary good distilled water. This treatment will also remove every trace of ammonia. Care must also be taken that the carbonic acid of the breath does not come in contact with the water while measuring with a pipette.

When the aluminum-mercury couple suggested by Ormandy and Cowhen* is used, direct nesslerization cannot be applied, for the separated alumina invariably holds a portion of the ammonia, and the results are too low. With caustic soda, however, at the end of the reaction, everything is in solution, excepting a slight residue of iron, etc., from the aluminum, and the portion nesslerized contains its full share of ammonia.

To determine how much aluminum must be dissolved to completely reduce the nitrates, the following experiments were made. The reductions were made in 50 cc. Nessler tubes, on account of the convenience with which large numbers of tubes can be handled in racks, and the ease with which they are cleaned.

Potassium Nitrate Solution.	Aluminum Grams.	Caustic Soda. 40% Solution.	Nitrate Unreduced	Nitrite.	Nitrogen as Ammonia.	Calculated Reduction.
1 part N. in 100,000	.01	1 cc.	82%	2.5%	15.5%	20%
"	.02	"	51.5	2.5	36.	36
"	.04	"	35.5	2.5	62.	59
"	.10	"	8.	3.0	89.	89
"	.20	"	0.	0.5	99.5	99
"	.40	"	0.	0.0	100.	99.99
10 parts N.	.01	"	80.	1.8	18.	20
"	.02	"	63.	3.0	24.	36
"	.04	"	39.5	3.5	57.	59
"	.10	"	15.	2.0	83.	89
"	.20	"	1.	1.0	98.	99
"	.40	"	0.	0.	100.	99.99
0.1 part N.	.02	"	32.	. . .
100. parts N.	.02	"	5.	. . .

The amount of nitrite present at any point is comparatively

*Jour. Chem. Soc., 1890, 811.

small, and disappears promptly when the nitrate is all reduced, thus marking the end of the action. If we assume that the first centigram of aluminum in dissolving reduces 20 per cent. of the nitrate, and each additional centigram 20 per cent. of that remaining unreduced, we obtain the figures given in the last column. These agree fairly well with the observed reduction. The proportion of nitrate reduced by insufficient amounts of aluminum is almost exactly the same, whether the standard contains 1 or 10 parts nitrogen as nitrate in 100,000. With more dilute solutions, the proportion is nearly the same, but with stronger solutions the ratio is lower, although the absolute amount of nitrate reduced increases.

With higher temperatures, the solution of the aluminum is much more rapid and a smaller portion of the hydrogen is effective. At 30°, each centigram of aluminum in dissolving reduces only about 10 per cent. of the unreduced nitrate, and so twice as much must be used to obtain a given reduction as is required at 20°. With temperatures lower than 20°, the action is very slow, and a long time is required for enough aluminum to be dissolved.

If a large excess of caustic soda is used, the action is also very rapid, and the hydrogen is less effective, but the difference is not so marked as when the action is hurried by increased temperature.

The time required for the action depends upon the surface of the aluminum; the form of the metal has no other influence on the reduction. The same ultimate result is obtained with equal weights of aluminum, other conditions being the same, whatever its shape. With thin foil, the reaction is complete in a few hours, while with thick wire, days may be required. When the tubes are allowed to stand over night at room temperature, foil 0.005 inch thick is thin enough, and gives less trouble by floating than thinner foil.

At one time we used a cheap caustic soda, containing zinc, because it was entirely free from nitrogen. It dissolved the aluminum freely, but for some unknown reason, the hydrogen evolved was less effective than that from other samples of caustic soda and potash. We thought this might be due to the zinc, but when zinc was added to pure caustic soda no corresponding effect was produced. The use of the soda was discontinued; but no explana-

tion of its action has been found. The presence of sodium carbonate, even in large quantity, does not affect the reduction in any way.

With a majority of waters, the aluminum dissolves much more slowly than in distilled water, or in solutions of potassium nitrate in distilled water. Whatever the cause of this phenomenon, its effect is to make the hydrogen even more effective than with potassium nitrate solutions, as is shown by the following result with a ground water in which the aluminum dissolved very slowly.

With .02 gm. Al.	0.45 part Nitrogen reduced.
" .10 " "	1.03 " " "
" .40 " "	1.03 " " "

The proportion reduced by insufficient aluminum is considerably greater than with potassium nitrate solutions in which the aluminum dissolves more rapidly. Care must be taken in such cases that enough aluminum dissolves. Conditions which are best adapted to the reduction of potassium nitrate often fail completely with waters, because in the time which suffices for the complete reduction of the standard, the reduction of waters with slow action is far from complete. As with the phenolsulphonic acid process, the fact of good results with standards is insufficient evidence of good results with waters.

The absence of nitrites, as shown by the sulphanilic acid and naphthylamine test, is the best evidence that reduction is complete. As long as a decided red is given by these reagents, we may be sure that reduction is incomplete, but when only a slight reaction or no reaction is given, reduction is complete, and no higher results can be obtained by dissolving more aluminum. To obtain this result with waters, in a moderate length of time, it is necessary to use twice as much caustic soda as is required by potassium nitrate standards.

To make the determinations of nitrates in waters, we proceed as follows: A 50 cc. Nessler tube is filled to the mark with the water, and about 0.4 gm. aluminum foil 0.005 inch thick added with 2 cc. of a 40 per cent. solution of caustic soda. After stand-

ing 18 to 24 hours at room temperature, a portion, 1 to 25 cc., depending upon the amount of nitrate present, is taken out with a pipette, and put in a tube of distilled water free from carbonic acid, which has previously been brought to the same temperature as the ammonia standards. All are nesslerized and compared in the usual way. Blanks and standards are frequently done as a control, and a portion of the waters, after reduction, is tested for nitrites. When nitrites are found in considerable quantity, the determinations are repeated, usually giving a higher result. In calculating the results, the correction for the volume of the caustic soda solution added, and the loss of ammonia with the hydrogen, and the reduction from ammonia to nitrogen, can all be combined in a single factor. When the determination is carried out as above, this factor is 0.88. Thus if 5 cc. of the reduced water contains 0.05 mg. ammonia, 5 cc. of the original water contained 0.88 of this, or 0.044 mg. nitrogen as nitrate. The blank should not exceed 0.005 part nitrogen in 100,000, and can often be neglected. Deduction is made for the ammonia and nitrites, but when the ammonia is a considerable fraction of the total nitrogen, it must be removed by boiling, after adding the caustic soda. In these cases, and also with waters having very low nitrates, especially yellow surface waters, the results obtained in this way are often unsatisfactory, both because the ammonia reading is influenced by the color of the water, and because the amount of ammonia obtained is too small for accurate estimation. In such cases 100 cc. or more of the water is boiled in a flask with the caustic soda to 50 cc. The reduction is then made as usual, after which the ammonia is distilled in a current of steam and nesslerized. If the water is concentrated in an evaporating dish, the results are high, owing to absorption of nitrous acid from the gas, but in a flask, the blank is not more than 0.003 part, and is quite constant.

The following determinations of nitrates were made by one of us, in solutions prepared by the other :

SOLUTION TAKEN.	Nitrogen as Nitrate Taken. Parts in 100,000.	Nitrogen as Nitrate Found.	
Potassium nitrate.	0.20	0.21	Direct reading
" "	1.52	1.48	" "
" "	0.68	0.72	" "
" "	1.76	1.67	" "
" "	0.96	0.92	" "
" "	1.46	1.50	" "
" "	0.0	0.0	" "
" "	1.20	1.20	" "
" "	0.06	0.05	" "
" "	0.25	0.25	" "
" "	0.010	0.009	Distilled
" "	0.044	0.043	"
10 Parts peptone0	0.013	"
10 " " with potassium nitrate	0.027	0.046	"
20 " "0	0.028	"
20 " " with potassium nitrate	0.030	0.049	"
10 parts egg albumen0	0.020	"
Sewage, albuminoid ammonia, 0.50	0.01	"
" " " 0.72	0.02	"

With large amounts of organic matter, the action of the caustic soda and aluminum decomposes a portion of the organic matter with formation of ammonia, as is shown by the experiments with peptone and albumen. As far as our experiments have been carried, this error does not exceed from 2 to 4 per cent. of the albuminoid ammonia. With almost all ground waters, and with most surface waters, this error is quite insignificant. It is only in presence of large quantities of decomposing organic matter that the result becomes uncertain. In such cases nitrates are invariably accompanied by nitrites, for if nitrate is added to such a water, a portion, if not the whole, is quickly reduced to nitrite, and in turn, the nitrite is often reduced, after all the nitrate is gone. We are thus able, in many cases, as for example with sewage, to infer the entire absence of nitrates from the low results, and the absence of nitrites. With excessive organic matter and the presence of nitrites, the results obtained can be taken as a maximum limit, and the same less 4 per cent. of the albuminoid ammonia, as a probable minimum limit. It should be observed that the nitrate determination in such unusual cases is of minor importance, and that the phenolsulphonic acid process is also quite unreliable under these conditions, the organic matters giving

a yellow color which often corresponds to more nitrate than is shown by the aluminum process.

With potassium nitrate solutions in distilled water, the results are quite satisfactory, being as accurate as the strength of ammonia solutions can be determined at a single trial by direct nesslerization, and we may believe that our results upon waters, with the above mentioned exceptions, are equally accurate.

LAWRENCE EXPERIMENT STATION.
MASSACHUSETTS STATE BOARD OF HEALTH.

SOME NOTES ON GLUCOSE DETERMINATIONS.

By FRED. C. WELD.

It is the custom in sugar house laboratories to clear dark-colored and impure solutions for polariscope work with subacetate of lead. A solution so cleared is useless for the determination of reducing sugars by Fehling's solution until the lead has been removed by precipitation and filtration. It is frequently convenient to store juices with subacetate of lead and use the solution so stored for determination of glucose (reducing sugars) and sucrose.

Hubert Edson* calls attention to the fact that a juice which has not been cleared reduces more copper than one which has. He publishes the following table :

Table No. 27.
Glucose Determinations in Basic Lead Acetate Solutions.

REMARKS.	GLUCOSE.		
	Basic Lead Acetate Added.	Basic Lead Acetate and Acetic Acid Added.	No Lead or Acetic Acid Added.
Clarified Juice	0.92	1.13	1.17
Syrup	2.99	3.49	3.76
First Massecuite	5.66	6.71	6.91
" "	5.47	6.50	6.35
" "	6.39	6.25	7.04
Second "	11.67	13.72	14.06
" "	14.86	17.73	17.29
" "	13.56	14.54	15.65
" "	13.54	15.21	15.47
" "	12.97	15.31	15.82
Final Molasses	17.54	20.15	20.93
" "	17.28	18.76	20.56
" "	16.87	19.04	20.45

*Calumet Sugarhouse Results. Campaign of 1889-'90, p. 31. Louisville, Ky. Courier Journal Job Printing Company. This Journal, 4, 381.

Edson further says: "The method pursued in the examination was as follows: The samples were weighed out, care being taken to have the same amount in each case. To the first was added basic lead acetate, solution made up to known volume, filtered, an aliquot portion taken, excess of lead precipitated, solution made up to known volume, filtered, and reducing sugars determined by Fehling's solution. To the second sample, basic lead acetate and acetic acid to acidity were added, solution made up as in the first, lead precipitated, solution neutralized and diluted to same volume as in the first, and reducing sugars determined. The third sample had no lead or acetic acid added, but was made up to the same volume in the same manner as the other samples. This last was taken as a standard, and the others were compared with it. The first method, it will be seen, gives an enormous error, amounting to about twenty per cent. of the reducing sugar present."

There are three possible explanations of the phenomenon noted by Edson: 1. Edson's own explanation* that the above mentioned variation is due to levulose compounds with lead; 2. Reducing substances, not carbohydrates, may be precipitated by the subacetate of lead; 3. The precipitant employed may make a difference in the correctness of the results.

To determine the action of subacetate of lead on invert sugar solution, refined sugar was finely powdered, washed with water, alcohol, and ether, and dried at 100 degrees for one-half hour. 9.5 gms. of this sugar were inverted according to Clerget's† method. The acid neutralized with Na_2CO_3 , and the solution made up to a liter. The glucose was then determined.

	I.	II.	III.
Without Pb	1.02	1.016 and 1.004	1.016
Pb and Na_2CO_3 added . .		1.004	.986

The results, while not checking exactly, are within the error of experiment, and show that no appreciable error is introduced by the addition of subacetate of lead to invert sugar solution.

Frühling and Schultz‡ have pointed out that there exist in the

*L. C., p. 30.

†Ann. Chim. Phys. (3) 26, p. 175; Ann. Chem. Pharm. 72, p. 145.

‡Anleitung zur Untersuchung für die Zucker-Industrie in Betracht kommende Rohmaterialien, etc., p. 97.

products of beet sugar manufacture substances, not glucose, which reduce Fehling's solution. I have been unable in any literature at my disposal to find any positive statement that such substances exist in cane products. Ferdinand G. Weichmann* says: "These methods of determining invert sugar (with Fehling's solution) are based on the assumption that there are no other substances present beside invert sugar which will precipitate the copper from its solution. Sometimes, however, such bodies are present. In beet sugar their existence has been amply demonstrated, and their presence in cane products is probable."

That such substances actually do exist in the products of the manufacture of the cane is shown by the following experiment:

3 gms. of molasses were weighed out and the glucose determined without the addition of any precipitant. The molasses showed 19.675 per cent. glucose. 15 gms. of the same molasses were boiled for half an hour with about 40 cc. of normal sodic hydrate, and determined in the same manner as the first. The reducing power of the molasses was now equivalent to 3.705 per cent. invert sugar. 15 gms. of Iloilo sugar (polarization $\pm 86^\circ$) were dissolved and made up to 150 cc., and the glucose determined—2.82 per cent. 30 gms. of the same sugar boiled half an hour with normal sodic hydrate, were made up to 150 cc. The sugar now showed a reducing power equivalent to .75 per cent.

These facts sufficiently account for the difference noted by Edson.

The following determinations of reducing sugars in the same sample of Iloilo sugar were made. 3 or 4 drops of subacetate of lead were added to the solution and precipitated in the usual way. The sugar then showed 2.73 per cent. glucose. 2 or 3 cc. of the subacetate were added, and precipitated when the sugar showed 2.61 per cent.

At this rate, even if all the substances which reduce Fehling's solution were precipitable by subacetate of lead (which is improbable), it would be impossible to remove them, in many cases, on account of the volume of subacetate and sodic carbonate necessary.

The precipitant may cause an error in two ways—either it may

*Sugar Analysis. John Wiley & Sons, New York, 1890.

invert cane sugar or it may decompose compounds of lead with reducing substances.

I am now engaged in studying the question of inversion.

A correct determination of glucose may be obtained by the method employed above, namely, by a redetermination after boiling with sodic hydrate. (See Frühling & Schultz and Weichman l. c.) The subacetate of lead does not interfere with this method.

The above determinations were made by titration with Violette's modification of Fehling's solution. (See, among others, Spencer's Handbook for Sugar Manufacturers, p. 59.) The end point was determined by Baswitz's method, which consists in laying two pieces of filter paper together and moistening one of them with the solution. The second paper receives a colorless solution, which is then treated with acetic acid and ferrocyanide of potassium. .05 cc. of Violette's solution may be easily detected in 50 cc. of water. This is the most convenient method of determining the end reaction of this titration, which has come under my notice. Tollens, however, remarks that it is not very accurate.

The subacetate was prepared according to Spencer's directions. (Handbook, p. 58.)

It will be seen from the above that there is no necessity to discard the subacetate, as Edson suggests, on account of its interference with the determination of reducing sugars.

As a clarifying agent, Edson admits that the subacetate is superior to the normal acetate, which he suggests as an alternative.

As a preservative, he finds the normal acetate satisfactory. Some experiments which I made in my laboratory confirmed the results of Edson in this particular. Some unintentional experiments, however, pointed to a very different conclusion.

Owing to lack of proper apparatus, I was obliged to store my subacetate in a loosely stoppered bottle; in the course of a week or two, under the action of the air, the oxide of lead was precipitated as carbonate, leaving a solution of the normal acetate. This solution, in several cases, failed to preserve the juices submitted for twenty-four hours to the high temperature of the sugar house.

ANIMAL, MARINE, AND VEGETABLE OILS USED IN LUBRICATION—THEIR CHEMICAL REACTIONS AND THE METHODS OF DETECTION IN MIXTURES.

BY PROF. THOMAS B. STILLMAN.

[Continued from page 218.]

Viscosity.

The viscosity or "body" of an oil is the first requisite in lubrication, and generally speaking, the best oil is one that varies the least in its viscosity as higher temperatures are reached.

The introduction, in late years, of a large variety of mineral oils of high viscosity for lubricating purposes, and the large number of compounds made use of to thicken these oils, has given this subject an enhanced value.

Standard simple oils, like lard oil, sperm oil, tallow oil, have a nearly constant variation in viscosity as the temperature of the oil increases.

The compounded mineral oils, containing thickening mixtures, "blown oils," etc., etc., present a different subject for examination, and no rule can be laid down for the increase or decrease of their viscosity at various temperatures, since many of the added substances show a high viscosity at normal temperatures and a very low one at high temperatures.

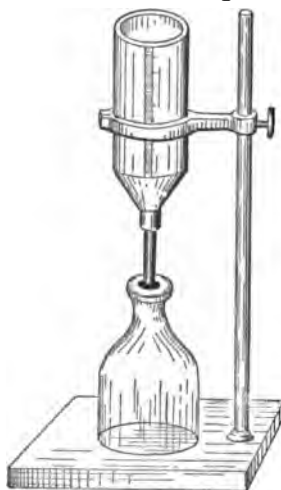


FIG. 3.

For this reason each sample of compounded oil should be tested for viscosity at various temperatures, and especially at the temperature at which it is proposed to use the oil in practice.

The first instrument for determination of the viscosity of oils was probably Schübler's (Fig. 3). It consisted of a graduated glass cylinder open at the top and drawn to a $\frac{1}{32}$ inch tube at the bottom. Having filled the cylinder with the oil to be tested, the time required for 100 cc. of the oil to flow out through the lower aperture was noted, and this figure compared with that obtained from water under similar conditions.

Thus, Schübler records, among many determinations, the following :

	Seconds at 15° C.	Seconds at 7.5° C.	Comparative Thickness with Water at 15° C.	Comparative Thickness with Water at 7.5° C.
Colza Oil	162.	222.	18.	22.4
Olive Oil	195.	284.	21.6	31.5
Hempseed Oil	87.	107.	9.6	11.9
Castor Oil	1830.	3390.	203.	377.
Distilled Water	9.	9.	0.	0.

The Penna. R. R. Co. viscosity tests are made as follows :

"A 100 cc. pipette of the long bulb form is regraduated to hold just 100 cc. to the bottom of the bulb. The size of the aperture at the bottom is then made such that 100 cc. of water at 100° F. will run out the pipette down to the bottom of the bulb in thirty-four seconds.

Pipettes with bulbs varying from $1\frac{1}{4}$ inches to $1\frac{1}{2}$ inches in diameter outside, and about $4\frac{1}{2}$ inches long, give almost exactly the same results, provided the aperture at the bottom is the proper size. The pipette being obtained, the oil sample is heated to the required temperature, care being taken to have it uniformly heated, and then is drawn up into the pipette to the proper mark. The time occupied by the oil in running out, down to the bottom of the bulb, gives the test figures. A stop-watch is convenient, but not essential in making the test. The temperature of the room affects the test a little. The limiting figures were obtained in a room at from 70° to 80° F. It will not usually be possible to make duplicate tests without readjustment of the temperature of the oil. Bullock & Crenshaw, 528 Arch St., Philadelphia, can furnish the pipettes for making viscosity tests. They should be ordered as "P. R. R. Viscosity Pipettes."

These pipettes are in use by many other railroads in the United States.

A. C. J. Charlier (*The Engineer*, 1890, p. 205) recommends the following :

"An ordinary glass tube having a diameter of half an inch, tapering to a point at one end, and marked into divisions of one inch, will answer all ordinary purposes for testing the viscosity of an oil. The oil to be tested is to be placed in this tube up to a certain mark, and is then allowed to run out at the tapered end of the tube, and the time taken is noted. This is compared with the time taken by standard oils previously ascertained in the same tube, and thus the viscosity of the oil can be determined."

W. P. Mason (*Chem. News*, 1884) describes a viscosimeter for use at 15.5° C.

The viscosity of an oil, experience has shown, should be determined at higher temperature than the above examples indicate.

Wilson's apparatus (Fig. 4) was one of the first where heat was applied to the oil in the viscosimeter. CREW, (*Practical Treatise on Petroleum*, p. 363).

A is a glass-tube about one inch in diameter, graduated from 1 to 100, to contain about 100 cc. of the oil. *BB* is a glass jacket about three inches in diameter, filled with water, as shown. *C*, a thermometer indicating temperature of water in jacket. *D*, a small brass cock for withdrawing water from jacket. *E*, a glass flask for generating steam to heat water in jacket. *F*, a glass pipe connecting the steam flask *E* with jacket *B*, delivering at bottom of jacket. *G* is a small cock for permitting an escape of steam in order to regulate the amount sent into jacket. *H*, a spirit lamp on a stand. *J*, a glass beaker to contain oil; and *K*, cast-iron stand, with adjustable arms, for carrying the apparatus.

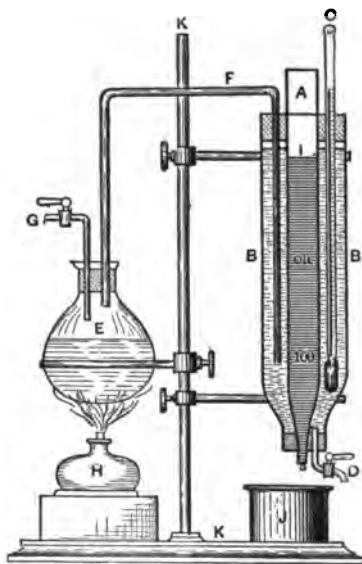


FIG. 4.

	RATE OF FLOW.		
	15.5° C.	49° C.	82° C.
Castor Oil	132	41
Tallow Oil	143	37	25
Neats-foot Oil	112	40	29
Rape Oil	108	41	30
Lard Oil	96	38	28
Olive Oil	92	37	28
Sperm Oil	47	30	25

Engler's viscosimeter (original form, Fig. 5) was constructed

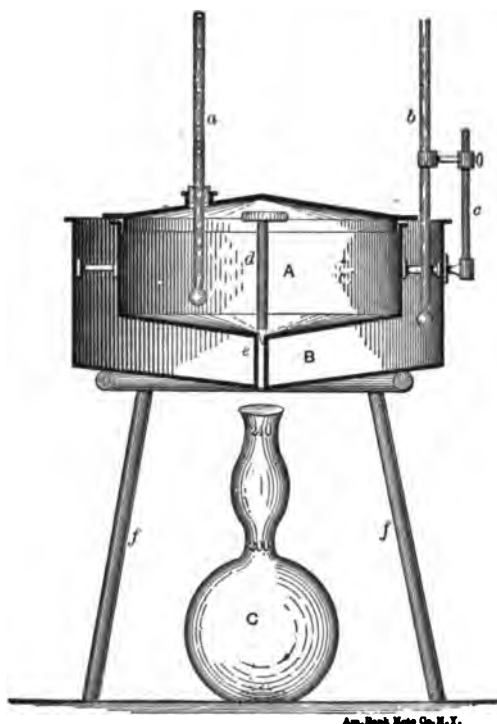


FIG. 5.

Amer. Bank Note Co. N. Y.

of metal, and consisted of *A*, a chamber holding the oil to be tested, *B* the water-bath, *C* a flask graduated so as to receive 200 cc. of the oil; *a*, *b*, thermometers; *c* the opening through which the heated oil flows out upon the withdrawal of the plug *d*.

In using this instrument the viscosity of an oil is stated in seconds required for 200 cc. of the oil to run into the flask *C*. Heat can be applied to the water-bath, and the viscosity determined at any temperature required up to 100 degrees C.

Engler recommends that all viscosities be compared with water, thus :

If water requires 52 seconds for delivery of 200 cc. into the receiving flask, and an oil under examination requires 130 seconds, the ratio is determined by $\frac{130}{52} = 2.50$, the oil thus having a viscosity of 2.5 times that of water.

This instrument has been for many years the one generally used in Germany for viscosimetry, and in its later form (Fig. 8) still remains so.

Boverton Redwood (*Jour. Soc. Chem. Ind.* 5, p. 128) describes a viscosimeter (Fig. 6), the general principle of which is the same as Engler's.

The tube *A* is of copper, and is $3\frac{1}{2}$ inches high by $1\frac{1}{8}$ inches wide. In practice, it is filled to a height indicated by the contact of the surface of the oil with a bent wire *B*. The orifice *C* is in agate. *D* is a thermometer; *F* and *E* the copper water-bath. The oil to be tested is maintained in the vessel *A* by a spherical plug inserted at *C*, which is withdrawn in the same manner as in the Engler apparatus. The bath is heated at *F*.

Redwood recommends the use of the two paddles for agitation and thorough mixture of water in the water-bath during the heating of the apparatus.

In practice, the viscosity of an oil is determined by the time required in seconds for 50 cc. of the oil to

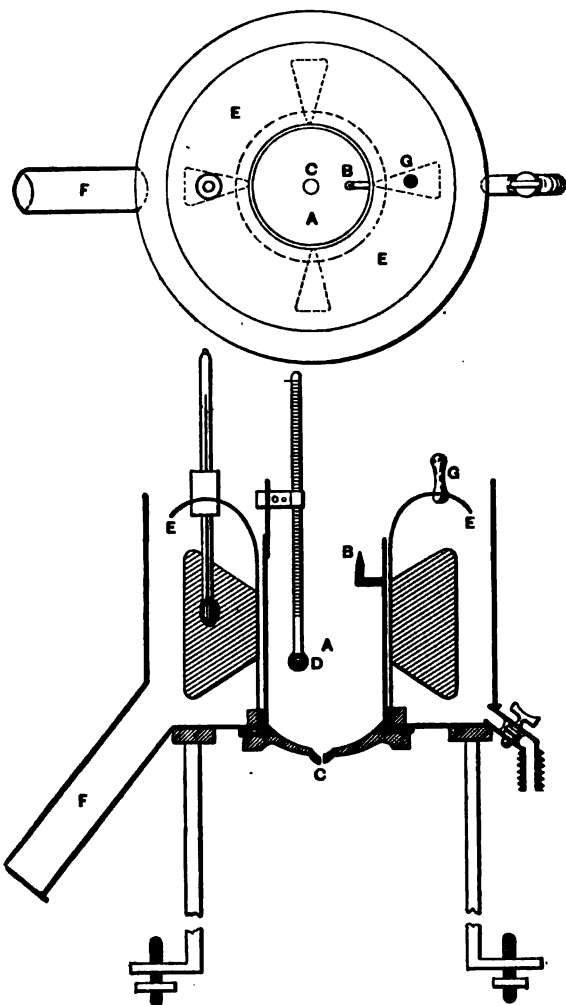


FIG. 6.

run into a containing flask placed under *C*. A number of determinations of viscosity at different temperatures by Redwood indicate as follows :

	At 15.5° C.	At 38° C.	At 94° C.
Rape Oil	540 seconds.	213 seconds.	58 seconds.
Sperm Oil	177 "	80 "	42 "
Neats-foot Oil	470 "	175 "	50 "
American Mineral Oil, sp. gr. .923 }	680 "	200 "	42 "

A. Künkler (*Ding. Poly. Jour.* **279**, 137) makes use of a modified form of the Engler apparatus to determine the viscosity at lower temperatures than normal, and also the solidifying point of the oils (Fig. 7).

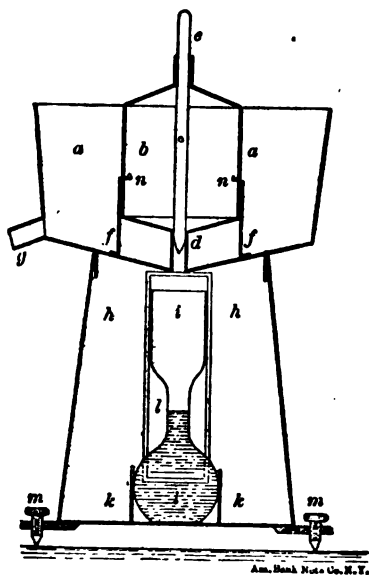


FIG. 7.

aa, instead of a water-bath, is a reservoir to contain a freezing mixture.

75 cc. of the oil are used, the containing mark being indicated by the points *nn*.

c, the delivery aperture, is 20 cm. long, 7 mm. wide, and is closed by the tube *e*, which passes through the oil and the upper portions of the viscosimeter.

The extension *g* is used to allow the liquid to run out of *a*, and is closed by means of a rubber tube and stopcock.

The upper portion of the apparatus rests upon the case *hh*, which prevents the warming of the outrunning oil at *d*.

50 cc. of the oil is run out into the measuring flask *i*, the latter being held in position by the supports *kk*. Two small windows, not shown in the drawing, are made use of in reading the delivery of the oil in the flask *i*.

Leveling screws *mm* are used to obtain a proper level in using the instrument.

The Engler Improved Viscosimeter is fully described in *Ding. Poly. Jour.* **276**, 42-47, by C. Engler and A. Künkler.

C. F. Cross, *Jour. Soc. Chem. Ind.* **9**, 654, in an abstract thus describes the apparatus (Fig. 8):

"The apparatus represented in Figs. 1, 2 and 3 has been designed to remedy the two defects of Engler's viscosimeter, viz., that in observations at high temperatures, the temperature of the oil varies sensibly during the running off, and the extremity of the efflux tube undergoes a gradual cooling.

It is an octagonal jacketed air bath, 35 cm. high and 20 cm. broad. The

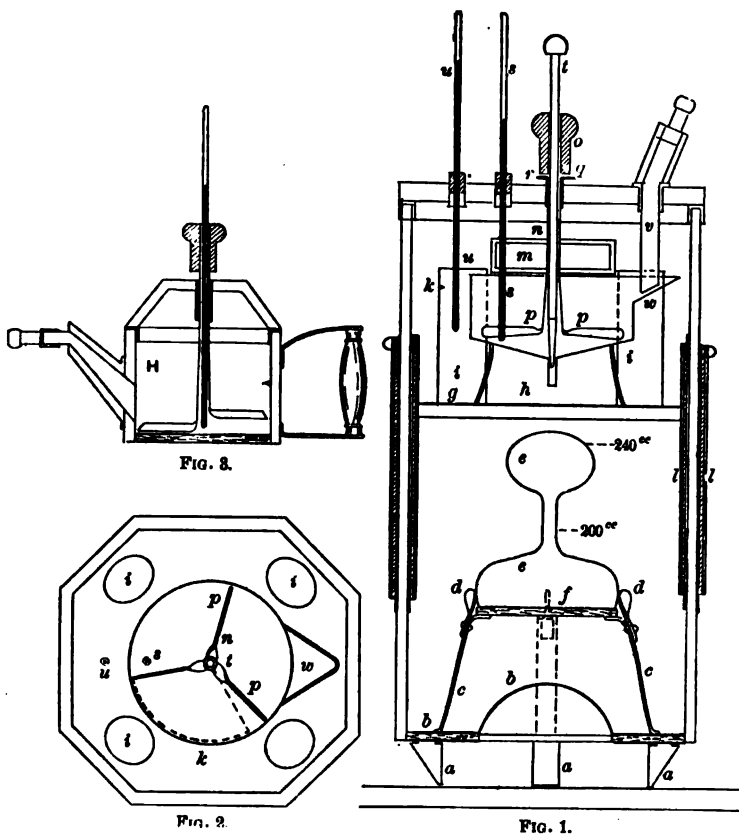


FIG. 1.

FIG. 2.

FIG. 3.

feet *a* stand in the ring of a tripod in such a way that the level of the bath can be adjusted so as to control the level of the liquid in the viscosimeter itself contained in the upper portion of the bath.

The heating surface *b* is arched; above this, and supported by the stand *c*, is the measuring vessel *e*, cut off from direct radiation from *b* by the asbestos plate *f*. Above this is the dividing plate *g*, upon which the viscosimeter is supported, the flow of oil passing to *e* through the opening *h*. Circulation

of hot air into the upper chamber takes place through *h*, as also through the four oval tubes *i* (Fig. 2). Through the cover plate pass the thermometers *u* *s*, the axis of stirring apparatus with the stop *l* for the efflux tube, and the funnel *v* for introducing the oil, heated to the required temperature in the apparatus *H* (Fig. 3). In the sides and cover, windows are let in the bath for illuminating, the former to permit observations of the level in the viscosimeter and the efflux of the oil into *e*.

That the instrument fully satisfies the required condition of constant temperature, is stated by the authors in the following terms: Up to 100 degrees, the temperature in all parts of the bath—heated with no change of oil in the viscosimeter—is equal and constant, excepting in the lower stratum of air in the viscosimeter itself, which is of course shielded from the general circulation. This difference disappears with the introduction of the oil. At temperatures higher than 100 degrees, the air above the viscosimeter is of somewhat lower temperature, but the difference at 150 degrees did not exceed 4 degrees.

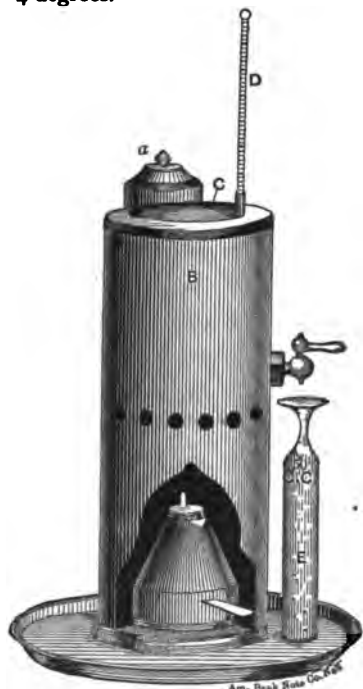


FIG. 9.

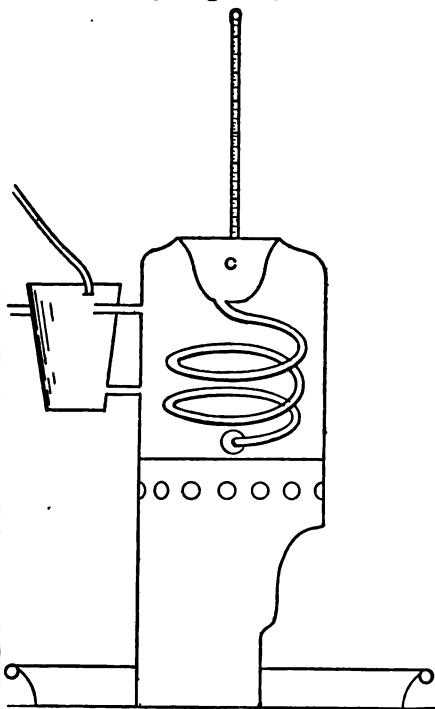


FIG. 10.

Tagliabue's viscosimeter (Figs. 9 and 10) consists of a basin *C* extending by means of the coiled tube to the outlet at the stopcock on the outside of the vessel.

This is surrounded by the water-bath *B*, which has an outer chamber *a* connected by two tubes, and in which the water is poured into the water bath. *D* is a thermometer, and records the temperature of the water-bath.

To test an oil, the water-bath is filled two-thirds full and heated by means of a small Bunsen burner or alcohol lamp. The top basin *C*, lined with wire gauze, is filled with the oil to be tested, and when the thermometer *D* indicates 100° C., the glass measuring flask *E* is placed under the faucet, which is opened with the starting of the watch.

When 50 cc. of the oil have run out and reached the mark upon the neck of the receiving flask *E*, the watch is stopped, and the number of seconds required noted.

The viscosity of the oil is stated in seconds.

This instrument has had a very extended use in the oil trade, but I have found it an exceedingly difficult piece of apparatus to clean when any particles of dirt have become lodged in the coil. This materially interferes with the flow of oil through the tube and gives false results. The basin *C*, as well as the coil, cannot be removed, as they are brazed to the water-bath. For this reason, and also when used at higher temperatures, the faucet being metallic and not heated to the temperature of the oil, the oil leaves the apparatus much cooler than the temperature recorded by the thermometer of the water bath.

Saybolt's Viscosimeter.—

This instrument, made use of by most of the chemists in the Standard Oil Company, is essentially as follows (Fig. 11):

"The oil to be tested is placed in the vessel *A*, which is enveloped in a bath of either heated oil or boiling water. The orifice through which the oil flows is at *O*.

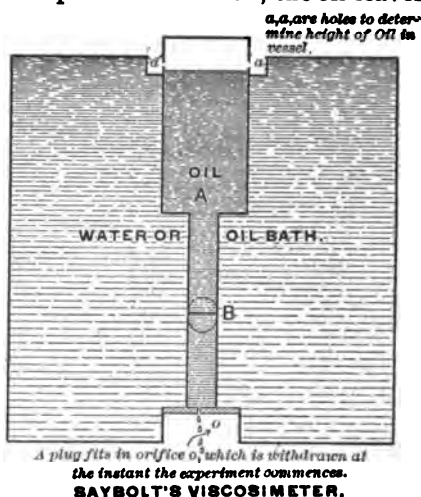


FIG. 11.

It is located somewhat above the bottom of the bath, in order that the oil, in issuing, shall not fall in temperature, as would be the case if the orifice was level with the bottom of the bath. (See also Engler's, Fig. 8.) The orifice is closed with a stopper, and the vessel *A* filled to the level of the overflow holes at *aa*.

The bath is then heated until the temperature of the test oil is at 100° C., or any higher temperature. The stopper is then withdrawn, and simultaneously a stop-watch is started. When the level of the oil in *A* has fallen to the mark *B*, set in a glass bulls-eye, the watch is stopped, and the number of seconds it records measures the viscosity of the oil. For instance, the time of flow of tallow, at 100° C., is fifty-five seconds. Hence, its "viscosity" is said to be 55. The quantity of oil which flows from the vessel *A* is about four cubic inches, or two ounces. The orifice *O* is $\frac{3}{64}$ of an inch in diameter. (Thompson & Bedford.)

Davidson's Viscosimeter (Fig. 12). [G. M. Davidson, Chemist, C. & N. W. R. R., Chicago, Ills.] This apparatus was designed, especially, for determining the relative viscosity of oils or greases when heated to the temperature of locomotive cylinders (250° to 350° F.). The entire apparatus, except the glass portion, is made of copper and the joints brazed.

The oil to be tested is put into the cylinder *A* and cup *R*, which are connected through the stop-cock *C*. The cylinder *A* is also connected with the glass gauge through the tubes *H* and *H'*, so that the height of the oil in cylinder can be seen. The bottom of cylinder *A* is covered by a brass plate, through which is bored a hole $\frac{1}{32}$ of an inch in diameter, which can be closed by the slide valve *E* held against the plate by a spring. The outside of the plate is beveled from the hole, so that the hole is in a very thin plate, and thus reduce lateral friction to a minimum. A long thermometer is used, so that the bulb will be near the bottom of cylinder *A*.

The cylinders *B* and *B'* contain the lard oil bath that is used for conveying heat to the oil in cylinder *A*. Heat is applied by a lamp or gas burner at the base of cylinder *B'*, and the hot products of combustion allowed to pass through the cylinder *G*. As the lard oil in *B'* becomes heated, it rises to the top of this cylinder, and passes over to cylinder *B*, down *B*, passing around the cylinder *A*, and back to *B'*, where it is reheated and recirculated, as shown by the arrows. The oil in cup *R* is heated by the products

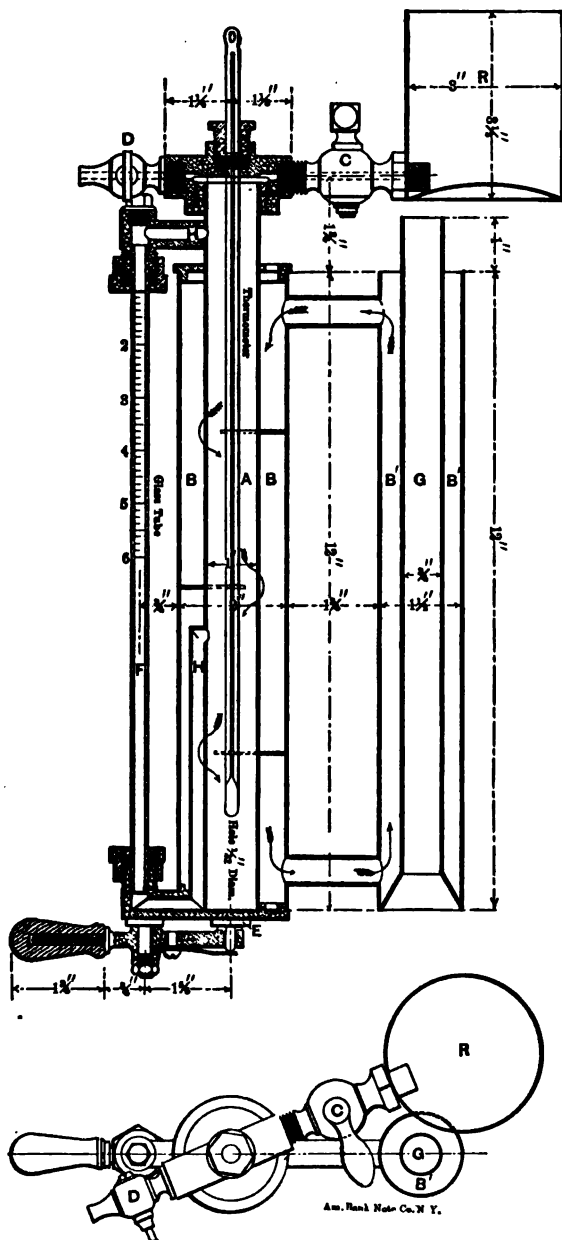


FIG. 12.

seconds required for this is the viscosity of the oil under examination.

[TO BE CONTINUED.]

of combustion escaping from the top of cylinder G, and in case of a high temperature by an additional lamp placed under the cup R.

When the oil under test in A and R has reached the desired temperature, the valve E is opened and the stopcock C is adjusted to keep the height of oil in A the height desired, as shown by the glass gauge. A 100 cc. flask, which is immersed in hot oil, is then placed under the stream of oil flowing from the hole, and a stop-watch is started the instant the oil commences to run into the flask. When 100 cc. has been delivered into the flask, the watch is stopped. The number of

HINTS TO BEGINNERS IN IRON ANALYSIS.

BY DAVID H. BROWNE.

WITH NOTES BY G. W. WHITE.

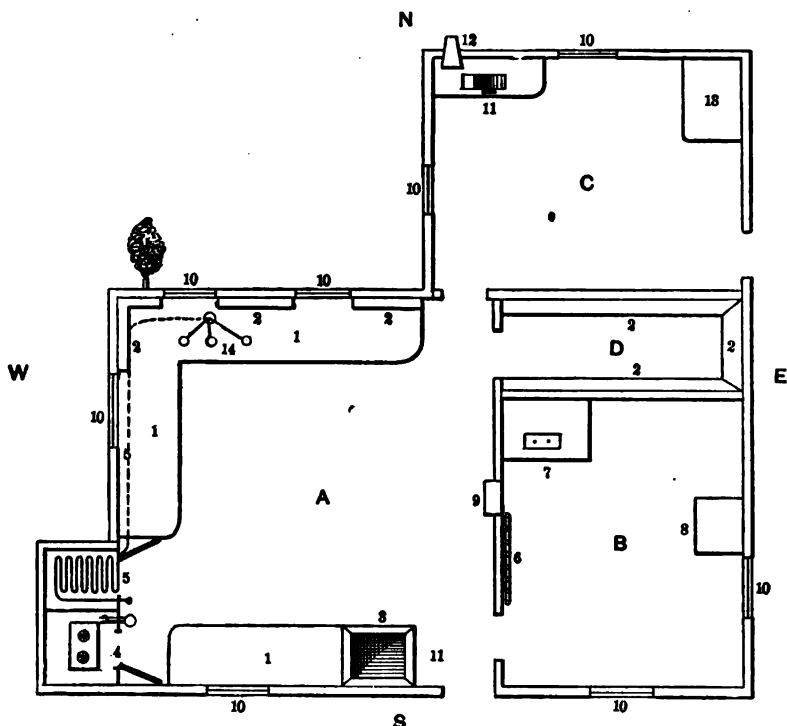
The popular appreciation of the value of exact chemical analysis as a standard and guarantee of the quality of certain products of the mine, furnace, and mill, has of late become widespread. There is, at the present time, more demand than ever before for the services of the analytical chemist. For the young and ambitious analyst, about to enter upon actual work, conscious of the practical deficiencies of even the best theoretical education, and of the lack of the caution and advice of some person of larger experience; for this beginner, in the hope that the suggestions here contained may prove of timely usefulness, these notes on the selection of apparatus, and the conduct of certain analyses, are especially designed.

The young analyst, arrived at the scene of his labors in some mushroom town in the mining region, is often expected forthwith to draw the plans and superintend the erection of such laboratory as he may require. His impressions of the actual needs of a chemical workshop, as derived from his memories of the building in which his previous training has been carried on, are often impractical and extravagant.

A suitable building is the first essential. The site chosen should be at a distance from stationary engines, steam pumps, and railways, sufficient to avoid vibration of the building, which would eventually ruin an analytical balance. A building 26 feet in length by 16 feet in width is large enough to give ample room, and small enough to keep the important item of expense well in hand.*

A plan which I have found very suitable, both for mine and furnace work, is here given.

*The building should be elevated from two to four feet above ground, to insure freedom from dampness, and to allow access to the water and steam pipes beneath the floor.



A. Main work room, 16 feet square; *B.* Balance room, 10x12 feet; *C.* Room necessary at mines for ore-grinding, etc.; *D.* Closet for glassware and chemicals; 1. Work benches; 2. Shelves; 3. Sink; 4. Gasoline stove; 5. Steam coil; 6. Steam coil for heating balance room; 7. Balance table; 8. Writing desk; 9. Chimney; 10. Windows; 11. Ore crushers; 12. Chute for throwing out ore; 13. Plate and rubber for crushing ore; 14. Filtering flasks.

The plan here given, containing three rooms, represents the laboratory as required for analytical work at the mines, where most, if not all the ore grinding, must be done by hand. The small room *C*, which may be built as a "lean-to" under part of the main roof, is then necessary. In it a small Blake or Gates ore crusher reduces the ore to the size of wheat, and fine pulverization is done on an iron plate or in a mortar.

The room *C* should, if possible, be detached from the main part of the laboratory, in order to prevent vibration from the mortar or crusher disturbing or injuring the balance. This may readily be

avoided by having the sill or frame upon which the room *C* is built made entirely separate from the main room. The floor beams should not be an extension of those of the main building, but entirely separate; so that the smaller room stands on a distinct flooring of its own.

Where power can be had, by shafting or belting from a machine shop, the ores may be crushed in a separate building near the source of power.

The working room should be at least twelve feet in height to the ceiling, as the fumes are otherwise very disagreeable. The sides of the large room *A* should be finished with narrow matched lumber, placed vertically, and ceilings of same material. Plaster is out of place in a laboratory; since the particles of lime and sand, loosened by the fumes of acids, are continually dropping on the work tables and spoiling analyses.

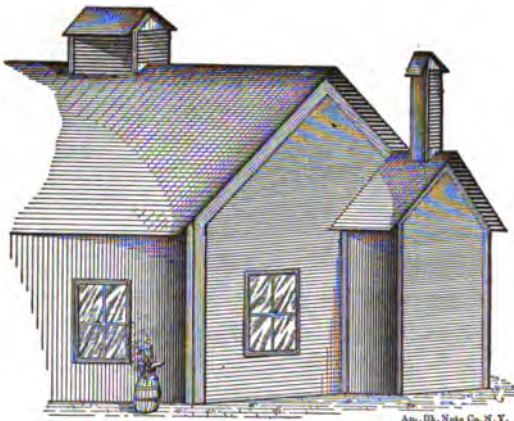
From the outer roof a ventilator, about 12 by 24 inches, rises a couple of feet and is connected with a similar opening in the ceiling of the working room. This is absolutely necessary in order to secure efficient ventilation. Ample light is needed and four windows in this room are none too many.*

The hood for evaporations is built to one side. This is three feet by six feet in size and projects from the gable of the building. It is lined throughout with matched lumber and divided into two equal parts by a partition of the same.

This hood is under an entirely separate roof; and is ventilated by a wooden chimney 12 inches square, which stands immediately over the central partition and communicates with both compartments. Two window sashes, hinged at the sides, and opening into the work room, give access to the steam coil and gasoline stove.

Three feet from the ground, scantling laid horizontally in this hood supports a wooden floor. On this a couple of inches of mortar is placed; and over this pressed brick are laid in regular order and the joints are filled in with cement. This forms a perfectly safe support for a gasoline stove; and is infinitely superior to wood in cleanliness and resistance to acids. As a protection against acid fumes, this hood is painted inside with the same asphalt

*The windows before the working tables should, if possible, be on the north side of the room to avoid direct sunlight.



PROJECTION SHOWING VENTILATION OF HOOD
AND WORK ROOM.

varnish used for the desks.

A small two burner gasoline stove is used in one side of the hood. The gasoline tank is placed outside the partition and in the working room, being connected with the burners by a pipe, bent at right angles, passing through the woodwork at one

side of the glass door. The precaution of having the tank outside the hood is necessary, since the fumes of evaporating acids would otherwise, in a very short time, attack the tin tank and perhaps cause a fire.

If coal gas can be had it is of course preferable; but at the majority of mines and furnaces gasoline must be resorted to as the best substitute. In the other side of the hood a steam coil is placed for evaporations not requiring so much heat. It is sometimes possible to have a steam-plate cast, and some may prefer to use this. An iron casting is made, about 12 inches by 18 and 3 inches deep, in shape somewhat like an iron kitchen sink. A lip about an inch and a half wide projects all around the upper edge. This upper lip is smoothed under a planer, and by means of bolts and nuts, passing through the lip, a plate of quarter-inch iron is secured on top, so as to form an air tight joint. Into the side of the casting two holes are cut and threaded to connect with steam pipes. With a pressure of a couple of pounds of steam this makes a very efficient heater; but the bolts are a continual source of leakage and trouble. After several years trial of both, I have a decided preference for a steam coil, as simpler and less liable to get out of order. This is easily made by having a dozen or more pieces of inch pipe cut to a uniform length of two feet four inches, and connected by means of return elbows at each end into the form of a

gridiron. This leaves a space of about half an inch between the pipes. On this the 8 oz. and larger beakers can safely stand; while for the smaller, a piece of thin sheet-iron, about a foot square, laid loosely on the pipes, is provided. A shelf at the back of this steam coil, and about 6 inches above it, on which such precipitations as lime and phosphorus can be left over night, completes the hood.

A closet is provided beneath the brick work supporting the steam pipes, for acids and ammonia. The steam pipes being above a non-conducting floor, do not heat this closet more than enough to prevent freezing of solutions kept therein in winter.

Around three sides of the main room are built working tables of inch boards, neatly matched, supported by legs of planed scantling. Three large drawers for filter papers, stirring rods, etc., are set under these tables. The height of the work tables should be such, that the operator's elbow, when he stands erect, comes about two inches above their surface. This is a few inches higher than the tables in common use in college laboratories; but with this height, the washing of precipitates, and the manipulation of reagents can be carried on without the tiresome necessity of stooping. A couple of coats of black asphalt varnish, which costs only sixty cents per gallon, makes a clean water and acid proof surface for the work tables.

The sink, which should be about 8 inches deep, is placed near the outer door. This should, in every case, be wood, not metal. An iron sink would last but a few months under the corrosion of waste acids, where a wooden sink, made of pine plank, mortised, and screwed together with leaded joints, will last as many years.

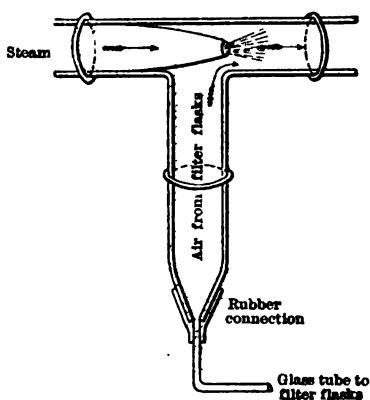
If running water can be had, so much the better. It often happens, however, that a tobacco pail with a faucet, standing on a shelf above the sink, is the only obtainable substitute. At the mines, even where hydrant water cannot be had, a pipe can often be led from one of the mine pumps; the water from which is often clear enough for general use. At furnaces a supply can always be obtained from the tank supplying the tuyeres and coolers.

The steam pipes should be supplied direct from the boilers, and

the main supply pipe should be protected by a coating of some non-conducting material. A wooden *launder* or trough, sunk a foot or so in the ground, and filled with ashes or boiler flue dust, in the middle of which the steam pipe is laid, will prevent condensation of steam, even in the coldest weather. A valve should be placed in this main pipe before it enters the steam coils.

A very good steam aspirator, much superior in cheapness and efficacy to any water pressure pump I have seen in the market, can readily be made at any blacksmith shop. A piece of one-half inch iron pipe is drawn to a tapering point, the opening in which should be about $\frac{1}{8}$ of an inch in size. This pipe is threaded a couple of inches from the point, and screwed into a common branch or T pipe, to such a distance that the point just barely passes the branch of the T.

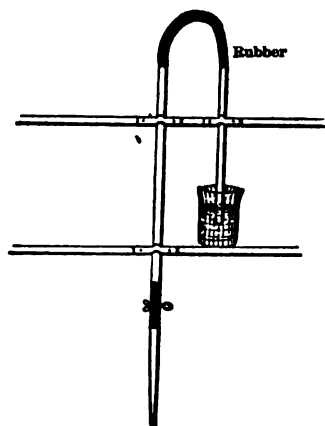
By screwing another piece of pipe into the other end of the T, and a smaller piece into the branch, an aspirator is made which, with very small amount of steam, will give a pressure equivalent to 10 inches of mercury.* The construction of the aspirator can readily be seen by the accompanying diagram.



A glass tube leads from this aspirator to a salt-mouth bottle, from which diverging rubber tubes make connection with three filtering flasks. A mercury manometer, easily improvised from a glass tube bent double, and containing a foot or more of mercury in the bend, is connected with the salt-mouth bottle, and by a scale attached serves to show at a glance any variation of pressure.

Shelves are placed above the table to suit the operator. Care must, however, be taken that the lowest shelf is high enough from the tables to allow a half-gallon acid bottle, generally used for standard solutions, to stand underneath.

*A piece of rubber tubing, slipped over the branch pipe from aspirator, and over which an ordinary glass carbon funnel is slipped, makes a handy reducer, for connection with tube running to the filtering flasks.



A stationary siphon, attached to the shelves, is often of great convenience in filtrations where pressure cannot be used. The sketch shows an easily adjustable form. By having a foot of rubber tubing forming the connection between the legs, the height of the shorter leg can be varied to suit the filtrate to be siphoned off. This is fixed above the aspirator, and is very quickly started by placing a beaker of distilled water under the shorter leg, and connecting the longer with the aspi-

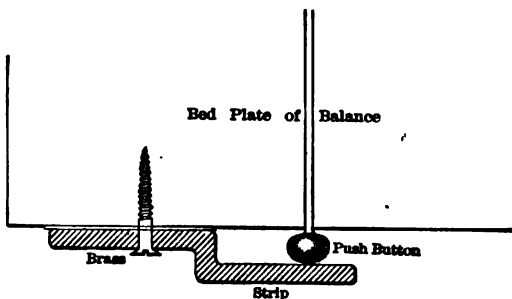
rator till the apparatus is thoroughly washed. The pinch-cock is then closed, leaving the siphon full of water, and the filtrates desired can then be siphoned off. When the operation is complete, a beaker of distilled water substituted for the filtrate washes out the glass tubes, and leaves the siphon ready for action again.

The balance room should have ample light; and the balance should be so placed that the light falls over the operator's shoulder. If the balance faces a window, reading of the smaller divisions on the beam becomes difficult. The selection of balance is, of course, a matter of individual taste, and the expense may be limited only by the operator's influence on the mining or furnace company.

After having used both Becker's and Troemner's, and after experience of both long and short arm balances, the author has found that Becker's No. 7 suits the requirements of general analysis better than a more expensive balance. The more expensive styles are a little too delicate for continual use; while the accuracy of the No. 7 Becker's balance for all practical work is unquestionable.

A little item in the selection of a balance, but more important than it might seem, must be noted. The pan arrest, worked by a push button from the front of the balance, should be provided with a spring catch to keep the arrest down, and allow the beam to swing. This little device saves much of the fatigue of weigh-

ing.* Some of the late short arm balances have a double door or hinged front, which is very unsatisfactory, causing vibration of the beam if the door be opened while the pans are swinging.



No improvement over the sliding front has yet been devised.

The balance room should be heated by a steam coil or radiator. A coal stove, with the attendant ashes and sulphur fumes, is entirely out of place in a balance room. To guard against acid fumes from the workroom the door should be fitted with a spring, or pulley and weight, to keep it shut.

A closet, marked *D* on the floor plan, is provided with several shelves to contain glassware and chemicals. This adds much to the neatness of the workroom and the comfort of the analyst.

In regard to gasoline lamps for ignitions and fusions the most serviceable in the market is that known as the "New Laboratory" lamp made by the Dangler stove Mfg. Co. of Cleveland.

The flame is rather large, but is under immediate control, as far as heat and volume is concerned. A heat sufficiently high for burning graphite in silicon determinations, is readily obtained with this lamp. For ignition of precipitates requiring a smaller flame, the Kellog gasoline lamp gives a flame which closely resembles that of a Bunsen burner. This lamp is the most satisfactory for the ignition of small precipitates such as BaSO_4 and $\text{Mg}_3\text{P}_2\text{O}_7$.

For the common analyses two glass stoppered burettes of 100 cc. and two of 50 cc. are required. These should be graduated to $\frac{1}{10}$ cc.† The best 100 cc. burettes in the market are about 42

*If the balance is not provided with this spring catch, a very simple and efficient substitute can be made from a thin strip of brass, bent as shown in the cut, and attached to the bed plate of the balance by a screw. When the push button is pressed, this brass strip is swung around till it covers the button and holds it in place during the weighing.

†It is always best to test burettes and make a table of corrections, for every 5 or 10 cc., thus:

Extremes. cc.—cc.	Factor between these extremes.	10 cc. =	Total value of max. reading.
0—10	.997	9.97 cc.	9.97
10—20	1.010	10.10 cc.	20.07

An operator who thus checks his burettes will find increased confidence in results, sufficient to repay the trouble.

inches long; this length giving ample room for the small gradations to be read.

Burettes of large caliber are a mistake, as the markings are necessarily so close together that accurate reading is out of the question. Floats are, in the majority of cases, a waste of time, as with good burettes accurate reading can be made without them. Trouble is sometimes experienced from leaking or sticking of glass stoppers in burettes. In such cases time and temper is saved by cutting the stop-cock off and attaching a fine drawn glass point to the end of the burette by a short rubber tube. A small plug of glass rod, to one side of which the rubber can be pinched, forms a valve more efficient and accurate than the glass stopper or pinch cock.*

A 12 oz. casserole, or handled evaporating dish, is very useful for iron titrations; and a 10 inch white porcelain plate is neater for color end reactions than any spotting plate with cavities in surface on the market.†

In pipettes, the only size absolutely necessary are a 200 cc. and a 50 cc. size. These are used in manganese determinations by Volhard's and Williams' method. Those graduated to deliver a certain amount are the most trustworthy and accurate.‡

In selection of glass-ware and apparatus, it is always necessary to bear in mind the uses for which they are required. Each analysis should be studied and the reagents and glass-ware required should be noted. Haphazard selections from a catalogue of such apparatus as the analyst thinks ought to be bought, without regard to necessity, generally results in the purchase of glass-ware useful only to encumber the shelves of the laboratory.

For analyses of iron ores, where a large number of phosphorus determinations are to be made, the beakers known as Griffin's form, lipped, are most convenient. Of these the 12 oz. size is used for solution of ores and evaporations to dryness; and the 5 and 2½ oz. size for the final precipitation of phosphorus. The 5 oz. size are also useful for solution of ore in the determination of iron.

*If the operator has time and patience, a little moistened emery powder may be placed on the stopper, which is then turned around in burette till a tight joint is obtained.

†Washing the plate directly after use and keeping it perfectly free from dust prevents the annoyance of the spots running together, which will often occur if the plate is wiped just previous to use.

‡Pipettes should always be tested and marked with both holding and delivery mark. The same mark will not answer for both cases. Where the delivery mark is used the last drops should not be blown out of the pipette.

The 20 oz. size of tall unlippped Bohemian glass beakers is the most useful for such large precipitations as iron and alumina in ores and lime in slags; while the 22 oz. is not too large for basic acetate work. Sizes larger than this are, as a rule, too fragile for service.

In flasks, the Bohemian glass alone should be purchased. One large flask, of a capacity of 3 liters, is very convenient for mixing molybdate solutions. Two flasks of two liters capacity are useful for heating distilled water; while the 16 oz. spherical flasks are the size needed for general wash bottles and filtering flasks. Two 12 oz. flasks, for dilute acid wash bottles, are convenient in the washing of small precipitates.

The triangular Erlenmeyer flasks are serviceable for filtrations, and avoid the necessity of using funnel supports.

For common analyses five wash bottles will be required. Two of these should contain distilled water, one dilute hydrochloric acid, one ammonia and one dilute sulphuric acid (1-50). The wash bottles used for ammonia and acid should be fitted with valves. That form described by the author in the *Journal of Anal. Chem.* for April, 1890, has the advantage of entire resistance to acid fumes; and requires less motion of the fingers to use than that made with a split rubber tube, as described by Mr. Blair in "The Analysis of Iron," page 24.

Distilled water, sufficiently pure for all ordinary mine and furnace analyses, can be obtained from a clean keg set under the steam escape pipe, by the side of the laboratory. If the pipes are some time in use and no oil be mingled with the steam, this water is exceedingly pure. For more accurate work, such as water analysis, this should be redistilled before using.

The selection of filter papers is an important consideration. The round cut filters manufactured by Schleicher and Schüll have become very popular, as they are sold in all necessary sizes. The best style made by this firm for general work is known as No. 597. These are especially valuable for pressure filtrations, being very rapid and reliable. The No. 595 filter paper is slightly cheaper, but not so quick working, nor as even in grade as the other.

Of the ashless or washed papers, that known as S. & S., No.

589, is most satisfactory. The ash of these can, in most work, be entirely disregarded. Filter paper No. 590 is a little lower in ash, but considerably dearer than No. 589. Since, however, the ash of a 589 filter of 9 cm. in diameter is .00011 gm.; and that of a 590 paper of the same size is said to be .00008 gm., the analyst can scarcely consider that a decrease of .00003 gm. in ash (a weight beyond the capacity of the average balance to register) is worth the increase of 35 cents a hundred in the cost of the latter papers.

As to sizes of filter papers, the 9 cm. No. 597 paper is most generally useful. This size is adapted for all such small precipitates as silica, lime, and magnesia, in ores, and silicon determinations in pig-irons; while for alumina and lime in slags, where 1 gm. is taken for analysis, the 12½ cent. papers are quite large enough; and for very small precipitates, such as magnesium ammonium phosphate, the 7 cm. size is required. For final filtration and ignition, these sizes of ashless papers will be needed; unless the operator prefers in every case to deduct the weight of filter ash.

In ordering funnels, care should be taken to obtain long-stemmed ground point funnels of an exact angle of 60 degrees. It is astonishing how few funnels conform to this apparently simple requirement; yet this is absolutely essential for safe and satisfactory use in pressure filtrations.

For 12½ cm. papers, a 2¾ inch funnel is required; while a 9 cm. filter requires a 2 inch and a 7 cm. a 1½ inch funnel. For such large filtrations as removing the zinc iron precipitate in Volhard's method, or for the final filtration of molybdate solution in Emmerton's titration of phosphorus, a 25 cm. E. & A. German white, or a Prat Dumas paper is necessary. These should be folded, ribbed, and used in a 5¼ inch funnel. At some steel works, the gray Prat Dumas paper is used exclusively for such work, and is very rapid, with the added merit of cheapness.

For pressure filtrations, two or three platinum cones, one inch in diameter, will be needed. Spun cones should be used, as the split cones, made from platinum foil, are liable to get out of angle and tear the paper.

For silicon and manganese determinations in iron and steel, a No. 5 evaporating dish is generally used. These are 4½ inches in di-

ameter, and require a 5 inch watch-glass to cover. A 6 inch dish is the size most convenient for the analysis of phosphorus by Emmer-ton's method. The style of dish which is most serviceable is that with round bottom, glazed inside, and rough half way up the out-side. These are less liable to crack than those glazed throughout.

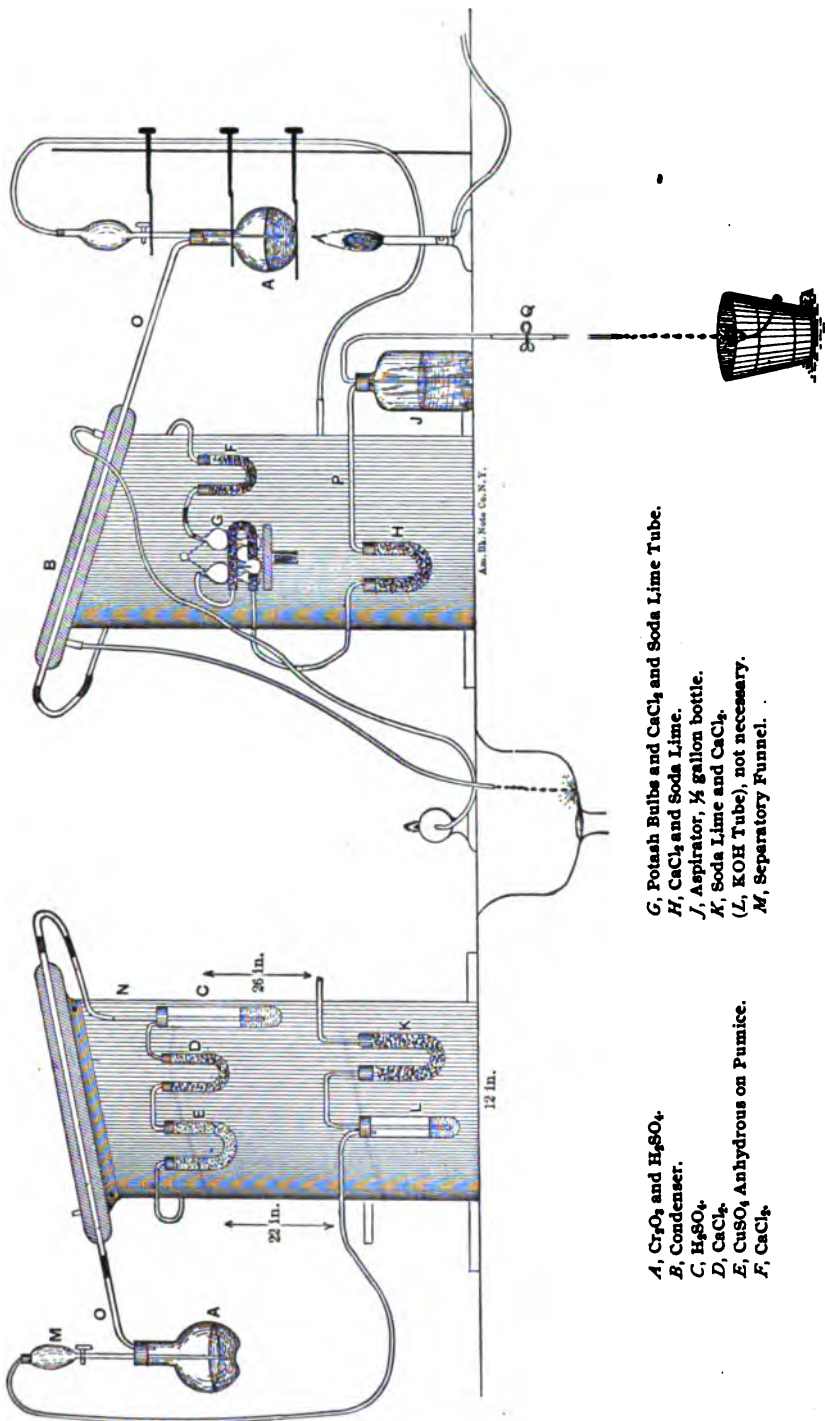
A fork in use at many of the larger laboratories, for handling evaporating dishes, is made by bending a piece of heavy telegraph wire into the shape shown in the cut.



This fits easily around a dish, and is invaluable where much evaporation is done. Two sizes are necessary for $4\frac{1}{2}$ and 6 inch dishes. For transferring the residue on an evaporating dish to a filter, the rubber spatula mentioned by Mr. Blair on page 25 of "The Analysis of Iron," is very convenient. Another handy instrument is made by bending a glass rod, about $\frac{3}{4}$ inch at the end, into a curve or semicircle to suit the dish, and covering this with a rubber tube.

It is sometimes necessary to set up an apparatus, of complicated construction, as for the determination of carbon in irons. In such cases it is very convenient to have the apparatus permanently attached to a support and in constant readiness for use. A very efficient method of arranging the usual carbon apparatus, and one which I have not seen described in print, is that devised by Mr. George Whyte, formerly Instructor in Physics and Metallurgy at Michigan University. This consists of an inch board fastened on a wooden base. The board is cut to stand 26 inches high at one side and 22 inches on the other. A couple of cleats on the diagonal upper edge support a condenser. The drawing of the apparatus, both sides being shown, conveys a clear idea of the convenience of this arrangement. The U tubes are fastened to the support by loops of copper wire passing through holes in the board.

The object of the H_2SO_4 tube at C is to retain any moisture carried through the condenser. By suction on the rubber tube, attached to the funnel M, the sulphuric acid is driven up the tube N. By compressing the rubber connections at any point a leak can be de-



A, Cr_2O_3 and H_2SO_4 .
B, Condenser.
C, H_2SO_4 .
D, CaCl_2 .
E, CuSO_4 Anhydrous on Pumice.
F, CaCl_2 .

G, Potash Bulbs and CaCl_2 and Soda Lime Tube.
H, CaCl_2 and Soda Lime.
I, Aspirator, $\frac{1}{4}$ gallon bottle.
K, Soda Lime and CaCl_2 .
L, KOH Tube, not necessary.
M, Separatory Funnel.

tected by the fall of acid in the tube. A very gradual lowering of acid may be disregarded, as due to gradual escape of water vapor from the tubes *D*, *E*, and *F*, under the partial vacuum produced by the suction. This will very slowly relieve the pressure; but a rapid fall of acid may be traced to a leak and remedied. It is very necessary to have a small U tube containing CaCl_2 in one leg and soda lime in the other attached to the potash bulbs and weighed with them. The small straight tube, designed to contain CaCl_2 , attached to the potash bulbs, is not sufficient to prevent the escape of a slight quantity of water from the potash solution.

In commencing analytical work the first and most important consideration, in regard to accuracy of results, is accurate sampling. At those steel works which make their own pig-iron, it is customary to analyze each cast of iron for silicon and sulphur, and every heat from the Bessemer converter for carbon. The average of a day's casts are analyzed for phosphorus; and a complete analysis is generally made of each day's steel from the converter.

The sampling of a cast of pig-iron, where very great accuracy is required, is best done by drilling a few gms. from the broken end of a pig, taken from the middle bed of the cast. A similar amount of drillings from a pig of the first and a pig of the last bed, mixed together, gives an average of the cast. For routine work, where all that is desired is to obtain a criterion of the working of the furnace, a sample drilled from the middle pig of the central bed gives a fair average of the cast. It is easily proved that silicon varies in the pig bed; being lowest in the lowest or first cast bed, and highest in the last bed nearest to the furnace.* The middle pig bed gives very nearly the average amount. The drillings in each case should be taken from the end of a freshly broken pig. If the end is rusted the first drillings should be discarded.

A convenient method of preserving the samples is to use manilla, or pay envelopes, opening at one end. On the upper end is written the consecutive or reference number of the analysis, and below the number or name of furnace, date and hour of casting, and grade of the metal.

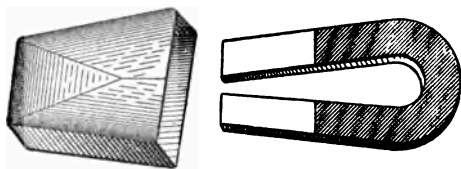
To clean these drillings, a magnet, with a cover of leather or stiff paper, is used.† By pressing the magnet into the cover or

*See this Journal 2, 148, 301.

†A small watch-glass is often preferred to a sheath over magnet. This is just as quick, and prevents drillings crawling up the magnet.

sheath, the samples can be lifted and shaken free from sand or dust. Then by slipping the magnet back, the drillings drop from the cover on a paper or watch-glass.

It is almost needless to say that these drillings should be taken with a clean drill. Where samples are sent in from a distance, and it may be suspected that the drillings are not clean, they should be washed with



ether to remove any traces of oil before analysis. For taking up small particles of iron, when weighing the samples, a pocket knife, having one blade magnetized, is very convenient.

At some furnaces it is customary to sample slags once a day. For this purpose, and in order to render slag more soluble in acid, it is best to catch a small sample in a ladle, as it runs from the cinder notch, and chill it by pouring into a scorification mould. This gives a chilled button of convenient size for analysis.* As each mould can be labeled and used for one furnace alone, there need be no confusion of samples.†

It is customary at most steel works to take from each heat a small sample for forge or hammer test. After this has been subjected to the required bending or forging, the heat number is marked upon it by a punch, and the bar thrown to one side for the carbon boys. These are drilled next morning, and about a gram of thin drillings placed in stout manila envelopes, numbered to correspond to the heats. After samples have been weighed for carbon, they are thrown together, a small amount put by for reference, part weighed for complete analysis, and the remainder thrown away. The envelopes are used again till worn out.

In iron mines, where both Bessemer and non-Bessemer ore is produced, the method of sampling must be determined by the conditions of the case. In each case, however, the demand is to keep every available ton of first-class ore separate from the second class. Where the ore is mined from rooms or chambers, record can read-

*Clemens Jones, in Trans. Amer. Inst. Min. Eng. 16, 89.

†At some furnaces it is customary to form a stopper of slag on the end of a long iron bar, for use in holding back iron when tapping. As this is made by dipping the rod into cinder buggies, and turning about till cinder is cool, and as this is done at each cinder flush, a good average sample may be had of the slag by breaking this stopper across the layers, and removing the inner layer, which may be contaminated by iron from the bar.

ily be kept of the grade of ore in various parts of that room; but where open pit work or stripping is used, the samples must be taken with reference to, and measurement from, some fixed point; as a shaft or derrick.

As an example of the methods employed in keeping track of the chemistry of an ore body, the method used by the author for several years at the Ludington mines of Iron Mountain, Mich., is here given.*

From each room in the mine, where ore was being broken down, samples of two to four pounds of ore were taken every week. These samples were obtained by pinching off small fragments of ore from all over the back or side of a room, where the men were working. In cases where a room was found to yield first and second class ores, samples were taken from each set of timbers in the room and analyzed separately, till the division of the ore into two kinds was located.

These samples were marked with the number of the room, level and shaft, and also the number of sets up from the level, and the location in the room of the sample. By reference to this direction the mining captain could separate into the several grades the ores coming from the mine.

Each skip or car of ore as it comes from the mine is marked, as to grade, by a wooden tag or label attached. A check on the underground sampling should be obtained by having the lander at each shaft take from every skip of first-class ore, a very small handful, which is placed in a box for daily analysis. During the shipping season analyses should be made of each day's shipments of Bessemer ore. This is readily done by having samples taken from each car by the men at the pockets, or by the brakesman at the stock piles. In this way a very close track of the accuracy of underground sorting can be kept and any error corrected.

To take an impartial sampling of an ore pile is not an easy matter. The most conscientious workman is apt, if not guarded by measurements, to favor the ore. Sampling by rule should in every possible case be resorted to.

A rope, having a knot made at regular distances of a foot, is a good substitute for a tape measure. This is stretched around a

*Trans. Am. Inst. Min. Eng., Vol. 17, p. 616.

stock pile, at the bottom, and from every place where a knot falls, a piece of ore the size of a walnut is broken or the same amount of fine ore is gathered up. Another sampling is made midway between top and bottom, and one at the summit of the pile. These samples are crushed in a Gates or Blake crusher, and quartered until a small sample is obtained.*

For final pulverization of ore, an iron plate and rubber, commonly known as a "bucking hammer," is very useful. With hard, gritty ores, some objection may be had to this, on the score of the iron being worn away and mixed with the crushed ore†; but with the usual soft hematites, the amount of iron thus removed from the plate is not sufficient to affect the accuracy of the analysis. Some ores may require a final rubbing in an agate mortar. Much of the fatigue due to the use of these small mortars may be obviated by using a piece of hard wood, about a foot square, in the centre of which an opening receives and holds the mortar. The pestle is also fixed in a piece of hardwood about 8 inches long, bored out at one end. This will be found a relief after the cramp usually resulting from the use of an agate mortar.

Passing from the physical side of analysis to the chemical, those points alone on which text books are not sufficiently explicit will be referred to.

In the selection of chemicals, great care should be taken to obtain only those of strict purity. For certain lines of work, however, the commercial acids will serve as well as the pure. For example, in routine analyses of silicon in pig-iron, where a large quantity of acid is daily used, the commercial acid will serve as well as any. In this case, the only precaution needed is the assurance that no insoluble residue remains after evaporation of the acid to dryness.

Again the purchase of zinc free from arsenic, or of potash made C. P. by alcohol, is often a needless expense. In each case the requirements of individual analyses must be studied; and it will be found possible in many cases to substitute a commercial acid,

*See this Journal V, 299.

†When hard silicious ores are crushed in an iron ore, the sample should be examined with a magnet for metallic iron, but as it is impossible by a magnet to separate metallic iron from magnetic oxide it is best to prevent the necessity for using a magnet by crushing the ore in a steel mortar of generous size.

worth three or four cents a pound by carboy, for a C. P. article worth 20 or 25 cents, in sealed half-gallon bottles. The operator must not, however, grow careless in the use of crude acids, for in most cases the C. P. is absolutely indispensable. Crude acids, such as the commercial hydrochloric, may be cleared of residue by filtration through asbestos when strong, or through filter paper where diluted with water.

The analyses most frequently required in iron are carbon, silicon, sulphur, phosphorus and manganese. In ores, iron and phosphorus determinations constitute probably two-thirds of the chemical work. For the analysis of iron in ores, a previous test as to solubility is necessary. If the amount of iron found in the ore, dissolved in HCl, is the same as found after fusion with alkaline carbonates, it may be taken for granted that all the iron in that ore is entirely soluble in acid. In such cases 0.5 gm. of fine ore is brushed into a 2½ oz. beaker, 15 cc. of strong HCl added and the covered beaker allowed to stand a couple of hours on a shelf above the steam coil.

Ferric chloride is liable to be carried off if the solution is too strongly heated. This can be shown by the reddening of a paper moistened with KCyS, held over a beaker of ore dissolving in boiling HCl. Again, a better solution is often obtained by slow action of acid at a low heat, the reduction to ferrous state is best effected by stannous chloride. Solution of this salt, which, by the way, when dry should be kept in the dark, is readily made by adding 25 gms. to a boiling mixture of one part HCl and one part water. If the solution remains milky a few gms. of flake or granulated tin causes ready clearance; and, if left at the bottom of the bottle, prevents reoxidation of the solution.

The stannous chloride is best added to the strong, hot, acid solution, drop by drop, from a burette. Any insoluble residue which may retain ferric chloride, should be stirred up with a glass rod. All the solutions should be reduced at the same time, and set to one side for titration. A very slight excess of SnCl₂ is all that is required, and no more should be added. The mercuric chloride should be added quickly; about 15 cc. saturated solution.

[TO BE CONTINUED]

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee reports the publication of the following works :

1. "Index to the Literature of the Butines and their Halogen Addition products (1863-1887). By Mr. Arthur A. Noyes, in the *Technological Quarterly*, Boston, for December, 1888.

This should have been noticed earlier, but owing to the absence of the author, now in Europe, it was overlooked. It comprises an author- and a subject-index; the abbreviations used are those of the Standard List prepared by this committee.

2. "Index to the Literature of Thermodynamics. Br. Dr. Alfred Tuckerman. Miscellaneous Collections of the Smithsonian Institution, No. 741. Washington, D. C., 1890, pp. vi-239.

This contains an author-index and a subject-index.

3. "Index to the Literature of Amalgams." By Prof. Wm. L. Dudley. In his Vice-Presidential Address to the Amer. Assoc. Adv. Science at Toronto.—*Proc. Amer. Assoc. Adv. Science* for 1889, pp. 161-171, 1890, 8vo.

4. "A Bibliography of Analytical Chemistry for 1888.—*Journ. Anal. Chem.*, iii, 1889.

5. The same for 1889.—*Journ. Anal. Chem.*, iv., 1890; and

6. "A Bibliography of Chemistry for the Year 1886." Smithsonian Report for 1886-'87. Washington, 1889.

These brief bibliographies are by Dr. H. C. Bolton.

7. "Professor A. A. Breneman, in a "Historical Summary to his Memoir on the Fixation of Atmospheric Nitrogen" (*Journ. Amer. Chem. Soc.*, xi), gives many bibliographical data.

The "Index Pharmaceuticus," published in the *Pharmaceutical Era* (monthly), and noticed in our sixth annual report, grows in scope and value. It is an alphabetical subject-list of original papers and important reprints and abstracts, appearing in thirty-two periodicals, English, American, French, and German. Although pharmacy is dominant, chemical topics are often included. The subject-index is followed by an author-index referring to the former.

*From advance proofs of the "Proceedings of the American Association for the Advancement of Science," vol. xxxiv.

The committee further report that several volunteer indexers are making progress. Dr. Alfred Tuckerman is engaged on an Index to the Chemical Influence of Light, and is planning more work of great value. Dr. James Lewis Howe is indexing the metals of the platinum group. Dr. H. C. Bolton reports progress on a Select Bibliography of Chemistry, which is an extension of the Bibliography of Historical Chemistry previously noticed; in the enlarged plan he is being assisted by Dr. Alfred Tuckerman.

As often stated in the annual reports, the Committee limits its duties to the encouragement of volunteer-indexers and to chronicling work performed. The fact that undertakings announced several years ago have not been recently noticed does not always indicate their abandonment; many will undoubtedly be brought to completion by their authors. Many chemists who are willing to contribute their quota to the general scheme are, however, deterred from making definite offers by the inadequacy of the libraries to which they have convenient access. This difficulty is a real one, and suggests that much might be accomplished by co-operation of several persons in a single subject, each indexing the sets of periodicals available, and submitting the partial work to one of the number for editing. In such an enterprise, conference between the several chemists uniting on a given topic would be necessary to avoid duplication and to secure a uniform plan.

Prof. W. O. Atwater, Director of the Office of Experiment Stations, Department of Agriculture, Washington, D. C., in conference with the committee, calls attention to the desirability of securing bibliographies and indexes to certain topics in the chemistry of plants and animals, such as (1) chemistry of albumenoid compounds; (2) chemistry of the so-called amid-compounds and kindred bodies; (3) chemistry of the fatty bodies; (4) chemistry of the lecithins, waxes, chlorophylls, chloresterin, etc.; (5) chemistry of the carbohydrates. These to meet a need which is being more and more keenly felt by physiological and agricultural chemists.

Subsequent to the presentation of this report, the Chemical Section authorized the insertion of the following minute:

After a discussion in the Section on the continuance of a committee to confer with others with a view to founding a National

Chemical Society, Dr. Albert B. Prescott suggested as a proper function of such a society the publication of an index to periodical chemical literature. He deprecated the multiplication of periodicals, and maintained the utility and importance of an index to the contents of those already in existence.

Respectfully submitted,

H. CARRINGTON BOLTON, *Chairman*,
F. W. CLALKE,
ALBERT R. LEEDS,
ALEXIS A. JULIEN,
JOHN W. LANGLEY (in Europe),
ALBERT B. PRESCOTT.

THE EXAMINATION OF CHINA TEAS.*

By P. DVORKOVITCH.

In view of the importance which proteine substances and tannic acid contained in tea have with regard to nutrition, it was of interest to investigate how far the value of tea depends on the content of the former. Does its value directly depend on the chief acting elements which, more or less, are contained in the tea?

This question has occupied the minds of many chemists. Mulder, Peligot and Claus started from the supposition that tea, like other plants which contain alkaloids, such as, for instance, peruvian bark, opium, and others, must contain more theine in its dearer than its cheaper qualities. But owing to the absence of exact methods for the determination of theine, they arrived at entirely contradictory results. Claus arrived at the conclusion that the older the tea leaf the more theine it contains. Meanwhile, the classical labors of Köllner, Makino, and Ogasvari,† on the study of the composition of tea leaves at the various periods of their development, plainly showed that the younger the leaf, the richer it is in theine and in proteine substance; and the older it is, the less of them does it contain. Thus, leaves gathered on the 15th of May contained 30.64 per cent. of proteine substances, and 2.85 per cent. of theine, while those gathered on the 30th of November contained 17.14 per cent. of proteine substances and 1 per cent. of theine.

*Communicated to the St. Petersburg Physico-Chemical Association, on the 4th-16th October, 1890. Communicated to this Journal by L. Loris, New York City.

†Landw. Versuchstation 33, 170.

Zöller proposed to determine the value of tea on the basis of the composition of its ashes. Relying on a single analysis of Himalaya tea, he arrived at the following conclusion: "The greater the amount of potassium and of phosphoric acid contained in the ashes, if they simultaneously contain a little lime, the dearer is the tea; if, however, the tea contains much lime and little potassium, it must be considered bad." Weyrich* made a whole series of experiments on ashes of tea, and arrived at the conclusion that "Zöller's method for determining the value of pure tea is useless, and can only be applied where there is a question of discovering falsifications in tea."

The Determination of Theine in Tea.—There are many methods for the determination of theine. They can all be brought under three categories.

1. *Peligot's Method.*—This method consists of the following: To the solution of tea, in the presence of an inconsiderable quantity of ammonia, lead acetate is added until no more precipitate is formed. The liquid is then filtered; the excess of lead removed by sulphuretted hydrogen; it is evaporated to a small volume and allowed to settle for twenty-four hours. The theine crystals which are deposited are again recrystallized, and the part of the theine which was left in the mother liquid is again titrated by tannin. This method is a very slow one, and the theine is, besides, very seldom obtained in a pure state.

2. *Mulder's Method.*—A decoction of tea is evaporated to the consistence of a sirup, calcined magnesia is added until alkaline, and it is then evaporated to dryness. The remainder is ground to a powder and extracted by ether until in the course of a few days the ether ceases to indicate on a watch-glass any traces of theine.

This method has been varied by many investigators, but the principle has remained the same, namely, a long heating of the extract with alkaline liquids. Some suggest the use of lime instead of magnesia; others have extracted with benzene instead of ether; others have used chloroform, heating not the decoction of tea, but the tea leaf itself.

Peligot has already pointed out the inexactness of this method. He observed that by this method ammonia comes off during the

*R. Weyrich, Ein Beitrag zur Chemie des Thees und Kaffee. Dorpat, 1872.

heating of the extract with ley. It is obvious that a destruction of theine takes place, and that less of it is consequently obtained.

Wakenröder plainly points to the destruction of theine under the influence of leys. By using Peligot's method, Weyrich found in a certain tea 2.25 per cent. of theine, but only 1.53 per cent. by using Mulder's method. True, Weyrich gives another explanation of this: he points out that by using Peligot's method, the theine obtained was impure. But this could hardly have had such an influence as to cause a difference of 0.72 per cent. In reality there is no doubt that by using Mulder's method a portion of the theine is destroyed. This explains why Weyrich, while using Mulder's method, obtained contradictory data, which led him to the conclusion that theine cannot be used as a means for determining the value of tea.

3. *Zoller's Method.*—In view of the contradictory results obtained by using the above method, Zöller worked out a method of his own. He moistens the dried and ground tea with oil of vitriol, mixes it somewhat, and warms it over a water bath until the cellular tissue is thoroughly dissolved. He then mixes it with water, treating the whole mass with 86 per cent. alcohol, and decolorizing the alcoholic solution with animal charcoal. During the evaporation, white crystals deposit. In order to obtain the whole quantity of theine, it is necessary to evaporate the mother liquor and to extract by means of ether.

In view of all these data, I tried to work out a method for the determination of theine for practical application, which would enable me to determine, exactly and quickly, the amount of theine in tea.

The method is as follows: 10 gms. of tea are carefully ground, and 200 cc. boiling water poured over it. Five minutes later the infusion is decanted. This operation is repeated three times. The tea is then boiled twice with 200 cc. water each time so that the water is not colored, or but very slightly so. The extract, rich in water, thus obtained, is diluted to one liter. A portion of this extract is washed with petroleum ether three times in order to remove the oil and the brown substance found in the tea. To this substance Mulder has already called attention.

Then, 600 cc. of this aqueous infusion, washed with petroleum ether, corresponding to 6 gms. tea, were taken 100 cc. of a solu-

theine, based on Mulder's principle, viz.: *on the boiling of the tea with magnesia or lime*, give always inexact results, always showing a less content of theine. This depends upon the theine being partly destroyed with evolution of ammonia. The degree of its destruction directly depends on the quantity of magnesia and lime employed, and on the time of heating.

THE PRODUCTS OF FERMENTATION OF TEA.

It was formerly erroneously thought that green and black tea belong to different species of plants. Their color depends on the way they are prepared; while for green tea the freshly gathered leaves are previously dried in the sun during two or three hours and then directly roasted in pans, the leaves for black teas are subjected to a preliminary fermentation which consists in the following: The freshly-plucked leaves are left on bamboo litters during 6 to 8 hours, they are then tossed in the air, then again collected in a heap, and again subjected to a further fermentation for a short time. Every planter has methods of his own for fermentation and they, of course, depend on his ability for their success. During this process the color of the leaf passes from green into brown which during the roasting turns into black. The destruction of tannin takes place during the process of fermentation. This was proved by Geissler's proximate analyses. He found the average contents of tannin in green Indian tea 16.38 per cent., but in black viz, in that subjected to fermentation, 11.54 per cent. This explains the more astringent taste of the former.

The quality of the tea, therefore, depends on the method of fermentation. Besides the disagreeable astringent action of the tea being thereby lessened, the fine aroma is obtained for which the China teas are so celebrated.

The process is entirely analogous with the fermentation of wine. From one and the same quality of grapes, under the same conditions of climate and soil wines entirely different in value are obtained. It is evident that during the process of fermentation the chief portion of the destroyed tannin must remain in the leaf itself, and to determine these products would, therefore, mean to determine also the degree of fermentation to which the tea leaf was subjected.

I have succeeded in working out a method which is applicable

not only to the determination of tannin in tea but which is also applicable to all substances wherein tannin is to be found. I have, by the way, also succeeded in determining the quantity of substances which are formed in tea fermentation.

The Method for the Determination of Tannin and the Products of Fermentation of Tea.—Many methods for the determination of tannin have been proposed. Looking, however, through the results of numerous investigations, we notice that these methods give even more capricious results than when theine itself is being determined. Löwenthal has worked out a method for the determination of tannin, which is based on the oxidation of tannin with potassium permanganate in the presence of excess of a solution of indigo-carmin.

The principle upon which Löwenthal based his method was correct but met with many difficulties when practically applied. It appeared first of all that the quantity of the potassium permanganate required for the oxidation of tannin depends directly on the rapidity with which it is poured in. The slower the addition of permanganate, the less will be requisite for the oxidation of tannin. The next difficulty was that the establishing of a titer for tannin is not always convenient since it is extremely difficult to obtain the pure tannin. Neubauer proposed to remove this difficulty by establishing the titer not with regard to the tannin but with regard to crystallised oxalic acid, whereby he found that 83 gms. oxalic acid correspond to 41.20 gms. tannin. I shall show hereafter that Neubauer found rather too high figures, because he probably established these data by oxidising tannin with permanganate quickly and not in the presence of indigo-carmin. In reality not the whole tannin, according to Löwenthal's method, is oxidised. If, for instance we add potassium permanganate after the appearance of the yellow color which serves to indicate the end of the reaction we will notice that for the entire oxidation a still larger quantity of permanganate is wanted.

For the determination of tannin is required :

1. A decinormal solution of pure oxalic acid.
2. Permanganate solution is prepared in such a manner that 130 gms. correspond to 100 gms. of decinormal solution of oxalic acid.

For this purpose 2.6 gms. are dissolved in one liter water and standardized.

3. About 50 gms. of the pure indigo-carmin paste, such as is usually used for microscopic work, is taken, it is mixed with water and 50 gms. of oil of vitriol is added to the solution, then about one liter of water, and the whole is filtered. The strength of the solution with regard to the permanganate, is so established that 25 cc. of indigo-carmin solution require 20 cc. of permanganate for their oxidation.

4. Sulphuric acid, (200 gms. oil of vitriol, to one liter of water).

5. A solution of caustic baryta (4 gms. to 100 cc. water).

The solution of tea (10 gms. to 1 liter water), was prepared by me as shown heretofore when determining theine. From this solution I took $\frac{1}{25}$ of the whole quantity, viz.: 40 cc., added to it, 500 cc. water, 25 cc. indigo-carmin, 25 cc. dilute sulphuric acid and titrated it with permanganate, until the yellow color appeared.

I must mention that the addition of permanganate was effected in the following manner. During the establishing of the titer of the indigo-carmin, I added about 18 cc. of permanganate, a 2 to 3 drops per second, and finally, one drop each time, until the appearance of the yellow color. But when titrating tea along with indigo-carmin, I added at once 23 cc. permanganate and then 2 to 3 drops each second, and at last one drop each second, until the end of the reaction. I have always taken care that the quantity of permanganate required for the oxidation should not exceed on the whole 38 cc. If it did exceed this amount, I took for the determination less of the tea solution mentioned. I had only either to take more of the solution or else to add the permanganate more slowly in order that the results obtained should be quite different.

I then took 80 cc. of the tea solution, added to it 20 cc. caustic baryta, and after filtering 50 cc., which correspond to $\frac{1}{25}$ part of the whole tea extract, I added 500 cc. water, 25 cc. solution of sulphuric acid and then the solution of indigo-carmin, and titrated it with permanganate in such a manner that at the beginning, when mixing, I poured in at once 18 cc., then 2 to 3 drops every second and finally one drop each second, until the appearance of the yellow color. *The quantity of permanganate thus expended*, on deducting the indigo-carmin which was required

for the oxidation, *indicates the quantity of the products of the decomposition of tannin, or more correctly, the degree of fermentation to which the tea leaf was subjected.* The longer the fermentation lasted, the more of these products.

The percentage both of tannin and the products of fermentation I calculate in such a manner that the amount of cubic centimetres of permanganate, spent on their oxidation, I convert to oxalic acid and then multiply by 31.30 as *I found that 63 gms. of oxalic acid correspond to 31.3 gms. of tannin* and not to 41.20, as found by Neubauer.

As already shown above, the establishing of the titer of permanganate in tannin is extremely difficult, I therefore resolved to establish the titer first in tannin, and then to establish at once in what relations permanganate stands to oxalic acid. I dissolved 10 gms. of pure tannin in water and, according to Hammer, noting the temperature, I found that the solution contains 4 per cent. tannin. From this solution I took 50 gms., corresponding to two gms. tannin and diluted to about one liter. For the experiment I took each time 25 cc. of this solution, 500 cc. water, and 25 cc. of solution of indigo-carmin, and added permanganate as shown above.

The results of the analysis :

1.	25 cc. solution of tannin	required	21 cc. of permanganate.
2.	25 "	"	20.9 "
3.	25 "	"	21 "

Consequently, 1 gm. tannin requires for its oxidation 420 cc. permanganate, which corresponds to 320 cc. of $\frac{1}{10}$ normal oxalic acid, viz.: 63 gms. oxalic acid requires for oxidation as much permanganate as is required for the oxidation of 31.30 gms. tannin.

I found my conclusion confirmed in the labors of the Meeting of German Chemists,* at which Schröder's proposals were accepted who introduced some alteration into Lowenthal's method. Schröder proposes to take indigotin instead of indigo-carmin. Schröder quotes, among others, a whole series of experiments, which show that the more rapidly the permanganate is added, the more of it is used, a fact which has also been established by myself. The author quotes the results of four experiments.

Experiment No. o.—To a mixture of tannin and indigotin, per-

*Ztschr. für anal. Chem. 1886, S. 121.

manganate was added, one drop each second, until the appearance of a light green color, and then 2 to 3 drops at a time, the liquid being mixed, until the appearance of a yellow color.

Experiment No. 1.—Permanganate was added at once, 1 cc. each time allowed, and mixed for 5 to 10 seconds, then, at the appearance of a light green-color, from 2 to 3 drops, as in Experiment No. 0.

Experiment No. 2.—Permanganate was added at once 2 cc. each time allowed it to mix for 5 to 10 seconds, and then on the appearance of a light-green color, from 2 to 3 drops, as in experiment No. 0.

Experiment No. 3.—Permanganate was added, 5 cc. at a time, and then it was added as in the preceding instances.

The results of these experiments he placed in a table :

No. of Experiment.	10 cc. Tannin equals 0.0017664 gm. Dry Tannin plus 20 cc. Indigotin. Required Permanganate.		For Tannin Permanganate was Required.	Obtained Dry Tannin.	The Relation to Oxalic Acid (cc. = Permanganate 0.003256 of Oxalic Acid.
	Each Time.	Aver'g.			
No. 0 (at 1 drop)	{ 18.1 cc. 18.2 " 18.2 " 18.3 "	18.2	7.5	0.002355	63:45.6
No. 1 (at 1 cc.)	{ 19.8 " 19.8 " 19.9 " 20.0 "	19.9	9.2	0.001920	63:37.1
No. 2 (at 2 cc.)	{ 20.5 " 20.3 " 20.4 " 20.4 "	20.4	9.7	0.001821	63:35.2
No. 3 (at 5 cc.)	{ 20.9 " 21.0 " 20.8 " 20.9 "	20.9	10.2	0.001732	63:33.5

From these experiments of Schroeder's it will be seen that with his method of titration not the whole of the tannin is obtained. Instead of 0.0017664 gm. of tannin he obtained in the fifth experiment 0.001732. But the relation to oxalic acid is 63:33.5, a figure closely approaching that found by myself.

As to the applying of indigotin instead of indigo-carmin I must say that the indigo-carmin which I have used in my numerous experiments always proved very pure, the change from light-green into yellow was always sharply marked and it presented no difficulties in handling. Its relation to permanganate in the course of two and sometimes for three weeks remained unaltered. By observing all the above mentioned details in working we are able always to obtain the most exact determinations of tannin.

I shall now explain the results of the following table of analyses of first crop China teas of the 1890 season.

Analyses of First-Crop China Teas of the 1890 Season.

TEA DRIED AT 100° C.

No of Tea.	Water.	Theine.	Tannin.	Products of Fermentation.	Extractive Substances.	Total Amount of Theine, Tannin and Products of Fermentation.	Their Relation to Each Other		
							Theine in Per Cent.	Tannin in Per Cent.	Products of Fermentation.
1	7.44	2.14	9.44	1.80	33.43	13.38	16.00	70.55	13.45
2	7.79	2.50	9.87	1.61	33.33	13.98	17.89	70.60	11.51
3	8.29	2.53	9.27	1.68	32.11	13.48	18.78	68.76	12.46
4		2.68	10.05	1.44	37.26	14.17	18.92	70.92	10.16
5	7.97	2.66	9.77	1.55	34.55	13.98	19.03	69.89	11.08
6	8.16	2.65	9.76	1.45	31.20	13.86	19.13	70.41	10.46
7	7.66	2.72	9.59	1.78	30.70	14.09	19.31	68.06	12.63
8	7.90	2.73							
9	7.91	2.86							
10		2.91	10.38	1.52	34.88	14.81	19.65	70.09	10.26
11	7.60	3.00	10.55	1.67	34.00	15.22	19.79	69.31	10.90
12		2.87	10.05	1.74	33.90	14.66	19.82	68.50	11.68
13		2.83	10.07	1.35	33.15	14.25	19.87	70.66	9.47
14	8.07	2.88	9.65	1.65	30.92	14.17	20.33	68.10	11.57
15		2.82	9.36	1.59	33.00	13.77	20.55	67.90	11.55
16		3.11	10.03	1.70	32.21	14.84	20.96	67.59	11.45
17	8.10	3.00	9.36	1.88	34.12	14.24	21.02	65.73	13.25
18		3.10	10.00	1.50	34.10	14.60	21.23	68.50	10.27
19		3.16	9.80	1.75	33.66	14.71	21.48	66.62	11.90
20		3.02	9.37	1.50	32.40	13.89	21.74	67.46	10.80
21	9.08	3.00	9.45	1.18	33.80	13.63	22.02	69.33	8.65
22	7.84	3.00	8.84	1.18	32.20	13.02	23.05	67.89	9.06
23	8.85	3.02	9.05	0.90	33.00	12.97	23.29	69.77	6.94
24	8.20	3.27	9.21	1.44	34.95	13.92	23.50	66.16	10.34
25	8.24	3.25	9.14	1.25	32.93	13.64	23.84	67.00	9.16
26	9.13	3.41	9.32	1.44	33.26	14.17	24.07	65.77	10.16
27	9.78	3.33	9.22	1.27	32.00	13.82	24.11	66.71	9.18
28	8.42	3.45	9.42	1.38	34.80	14.25	24.22	66.10	9.68
29	7.83	3.21	9.00	1.17	33.46	13.38	24.52	67.26	8.22

From the above table we see that in the best qualities the proportion of theine is increasing, but this is manifested even more strongly when we take the ratio of theine to the total amount of tannin and products of fermentation in tea.

Let us take as an instance the teas No. 11 and No. 22; their contents of theine are at the first glance equal; but in reality these teas are of quite different quality. We have only to look at their relation to each other in order to notice that there is between them a great difference. In the tea No. 11 the ratio of theine to the total amount of tannin is equal to 19.76 per cent., but in the tea No. 22 it equals 23.05 per cent.

Consequently the greater the ratio of theine to the total amount of tannin and products of fermentation, the dearer the tea. The more regular the fermentation the better the tea. The regularity of the fermentation is recognized by the relative amount of products of fermentation in tea.

I hope shortly to be able to communicate in detail the results of the investigation of these products.

A NEW FORM OF AIR BATH.

BY F. R. BENNETT.

The air bath here described is the design of Mr. Maunsel White of the Bethlehem Iron Co. It has been in use for several years, and has proved so convenient that it seems worthy of description.

In the accompanying cuts is shown a general view and section. In Fig. 1 *a* is a hole through which a thermometer is inserted, two holes to either side not shown, permit the escape of the gases of combustion. *b* is a door having double panes of glass, about one-fourth inch apart, forming a non-conducting air space; around the door is fastened a flanged strip of sheet copper, which makes a lip that fits tightly into the bath, serving to keep the door firmly closed and excluding the air; another similar door is placed at the back which is not shown in the cut; *c*, is a pivot on which the bath may be revolved without interfering with the flow of gas. *d* is the combustion chamber, the sides of which are open,

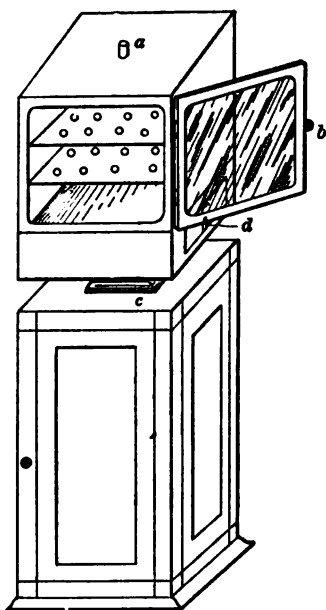


FIG. 1.

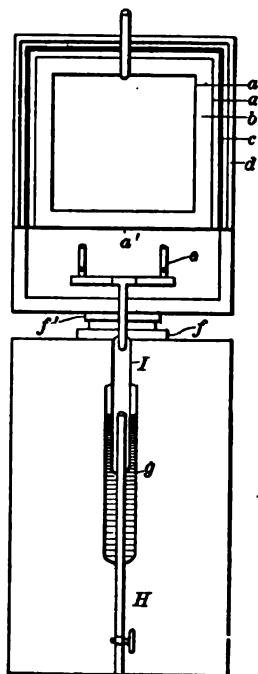


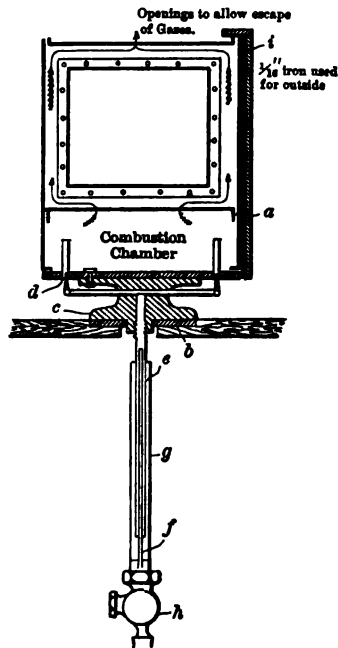
FIG. 2.

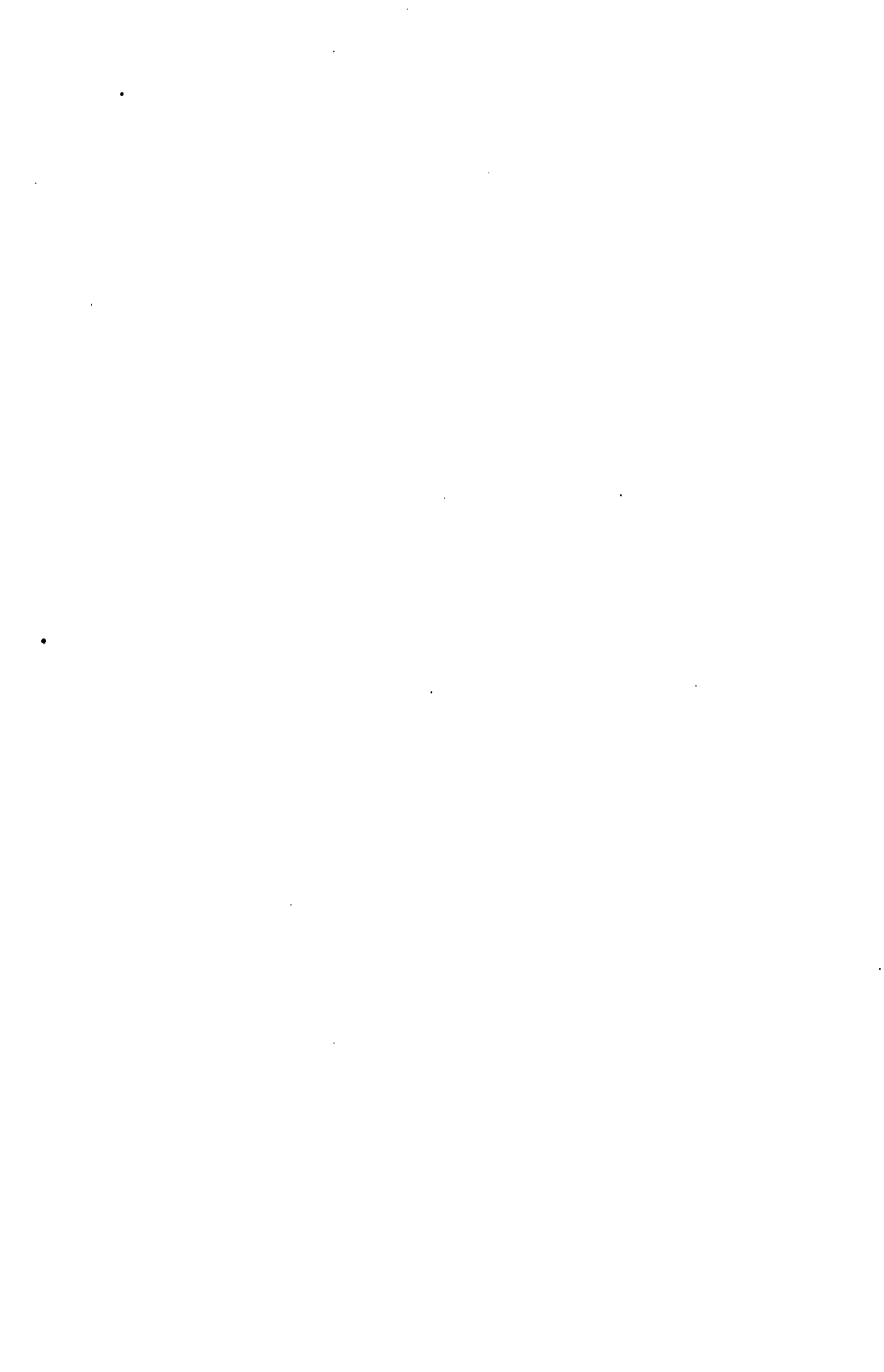
but protected with flaps of asbestos board. In Fig. 2 *a* is the baffle plate with holes to permit heated gases to pass around copper box of bath; *b* is a brass disc let into wooden frame to hold bath central and give plane of rotation; *c* is a brass support fitted with two branch pipes to supply gas. The support is securely bolted to the one-fourth inch iron plate which forms the bottom of the combustion chamber; *d* are openings around jets to supply air for combustion; *e* and *f* are brass pipes fastened to the globe joint *h*; *f* is the supply pipe, and passes up into *e*, which is secured to *c*; the outside box of bath, is made of one-sixteenth inch sheet iron; *g*, is filled about three-fourths full of oil, making a gas sealed joint. The advantages of this bath are, better utilization of heat, uniformity of temperature throughout the bath, and ease and convenience of manipulation. I am indebted to Mr. White for a drawing of the bath and explanation of its working.

LABORATORY BETHLEHEM IRON CO.

ERRATUM.

The wrong cut was by mistake printed as fig. 2, on page 356 of the June number. Please cut out the annexed figure and paste it over figure 2.





NEW BOOKS.

"Die Untersuchung Landwirtschaftlich und Gewerblich Wichtiger Stoffe."—Verlag von Paul Parey. Berlin.

"Examination of Materials of Importance in Agriculture and Commerce" is the title of a book just published by Paul Parey, in Berlin, of which Dr. J. König, Director of the Agricultural Experiment Station in Münster, is the author. It was the intention of Dr. König, in the commencement of this work, to re-edit the third edition of Wolff's treatise, "Instruction to the Examination of Materials of Agricultural Importance" which was published in 1885. In the prosecution of this work, however, the necessity of introducing so much new material compelled him to abandon his attempt at simply rewriting Wolff's book and to make of the volume a new work.

The book comprises nearly eight hundred pages of rather fine print and treats of the methods of the examinations of soils and agricultural products, both from a physical and chemical point of view. In addition to this, the method of microscopic examination of the most important food products is also given.

The methods which are described for the analytical processes are those which have been generally approved by the experience of the analysts in Europe, and the subject is brought down, as far as European literature is concerned, to the beginning of the year 1891.

An excellent resume is given of the various methods which have been followed in the physical analysis of soils, which, however, is rendered of less value because of no allusion whatever to the excellent method of Osborne which was founded on the older method of Bennigsen, a method which is far superior to all others for accurate and rapid silt analysis.

The various methods of determining the porosity of the soil, its absorption power and its deportment toward water and various saline solutions are also described briefly but succinctly; but no mention is made of the valuable work of Whitney and King on these points.

There is also an article, of much interest for agricultural purposes, on the estimation of limestone, cements and clays.

The methods practiced in Europe for the analysis of stall manure, guano, bone, superphosphate, etc., are described in full; likewise is given a full description of the European methods of milk, butter and cheese analysis.

The chapter on the analysis of sugars and sirups is also brought down to the latest European investigations.

The chapter on the analysis of the material used in breweries and the waste products of distilleries is, of course, of more interest to European than American agriculture. In Europe the number of distilleries is very great, and their relation to agriculture is very intimate. In this country the number of distilleries is very small, and their capacity proportionately larger than those of Europe. As a result of this, the brewing and distilling interests of this country are occupations which apparently have little relation to its agriculture.

Dr. König has shown the same admirable qualities in the arrangement of this work which have been noticed in his other works which are of such indispensable value, not only to European, but also to American agricultural chemists. The most striking defect of the work,—one, however, which would not be noticed in Europe,—is the entire absence of any allusion whatever to American investigations in agricultural analysis, save the brief statement concerning the Hilgard process of elutriation, which is dismissed with the sentence that it is too little known in Europe to demand further description. During the eight years, however, in which the Association of Official Agricultural Chemists in this country has been engaged in the study of processes of agricultural analysis, most important improvements have been elucidated for the various methods of examination of the substances which have been studied, and it is somewhat surprising that in a book, of the magnitude of König's, no allusion whatever is made to the work of our Chemists' Association. As a result of this failure to notice the work of the American chemists, many erroneous processes are described in the work which might have been omitted or corrected if due attention to the published proceedings of this Association had been given. For instance, in the method for the optical examination of milk, the old process of precipitating the al-

buminoids with basic lead acetate is recommended, although it was shown many years ago, by the Chemical Division of the Department of Agriculture, that this method was essentially erroneous and that accurate results were obtained by the use of acid mercuric nitrate or mercuric iodide with acetic acid.

The difficulties attending the separation of the ether solution in Soxhlet's areometric method for the determination of milk was fully described in some of the earlier papers read before the Association of Official Agricultural Chemists, and also in a paper presented at the meeting of the American Association for the Advancement of Science in 1886. The method of overcoming the difficulties, which was described at that time, is credited in König's work to a European investigation of two or three years later date. The accurate and rapid methods for the estimation of fat in milk, which have been described by Babcock, Patrick, Cochran, Parsons and Short, are not so much as mentioned in the chapter on the analysis of dairy products; yet these methods, when properly carried out, lack nothing in accuracy and are very much easier of execution than many of the old methods which have been employed. In like manner the method of determining the melting point of butter and other fats, now in general use among our Agricultural Chemists escapes without mention.

The chapter on the estimation of phosphorus, nitrogen and potash in fertilizers, seems strangely crude to those who have become familiar with the accurate and thorough methods which have been adopted by the Association of Official Agricultural Chemists.

The workers in European agricultural chemistry are apparently unaware of the fact that we have in this country a body of men quite equal to them in ability, and almost equal in number, who have been devoting many years of most serious study to the improvement of analytical methods and whose work seems to be totally unknown to investigators beyond the Atlantic. While these defects in König's book would render a translation of it into English, for the use of non-reading-German American chemists, if any such there be, of no value, yet the work possesses so many points of merit as to make its possession a matter of the greatest importance to American workers.

H. W. W.

Ramsay's Inorganic Chemistry.*—This book shows, even to the casual reader, that great care has been taken in putting it together; it shows as well that the writer is competent for the work and that his knowledge of the subject is both broad and deep. It is one of the best books, and will be an excellent laboratory companion for advanced students. E. H.

Blair's Chemical Analysis of Iron.†—The first edition of this valuable book has been out of print for some time. The new edition needs little comment. For the chemist concerned with analysis of iron it may well be considered indispensable. The new edition follows in the main the original lines, but contains many additions and emendations,—such as the description of Mr. Maunsel White's Agate Mortar operated by power, the determination of carbon in steel, etc. E. H.

NOTES.

Labelling Chemical Glassware.—It is frequently desirable to attach a label to beakers and other vessels employed in analytical work, and gummed, blank paper labels are often so used, but with some disadvantages. A very satisfactory substitute is obtained by "grinding" a portion of the surface of the glass in the following manner: An old knife blade or spatula is wetted with a solution of sodium hydrate and dipped into ordinary emery flour; this is rubbed upon the convex surface of the glass, so as to roughen a patch about one-half inch square. Upon such patch one can mark with a pencil, and when washing the vessel such marks are readily removed. After a little practice one may easily so put ground patches upon a nest of six beakers in ten minutes. —F. P. Dunnington, *Chemical Laboratory, University of Virginia.*

ERRATA.

Page 282, May Number, 23d line from top of page, for "*an excess of hydrochloric acid is an important condition,*" read "*an excess of sulphuric acid is an important condition.*"

By mistake, the abstract of Stutzer's paper on "*The Estimation of Nitrates by Aluminum,*" Vol. V, p. 225, was made to read the opposite of what the author intended. It should be "*Metallic aluminum made by the old process is preferred by the author, the trace of sodium remaining causing more rapid solution of the aluminum.*" J. B. W.

**A System of Inorganic Chemistry.* By William Ramsay, Ph.D., F.R.S. Prof. of Chemistry in University College, London. 800 pp. xv, 700. Phila., P. Blakiston Son & Co.

†*The Chemical Analysis of Iron.* A complete account of all the best known methods for the Analysis of Iron, Steel Pig-Iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By Andrew Alexander Blair. 8vo pp. 314. Phila., J. B. Lippincott Co. \$4.

===== THE =====

Journal of Analytical AND Applied Chemistry.

HINTS FOR BEGINNERS IN IRON ANALYSIS.

BY DAVID H. BROWNE.

WITH NOTES BY G. W. WHITE.

[Continued from page 342.]

If HgCl_2 be added slowly, the first portion added is reduced to metallic mercury by the SnCl_2 , and remains as a black precipitate, vitiating the results of titration. A slight, silky precipitate of mercurous chloride shows that tin chloride was in sufficient excess;* an excessive precipitate interferes with the color of the end reaction. The solution of mercuric chloride should not be added till just before titration, since the ferrous solution, which might stand for half an hour without oxidation after the SnCl_2 has been added, commences to re-oxidize after excess of tin is removed by mercury. The ferricyanide indicator should be freshly made and very weak; a grain about as large as a pinhead in 20 cc. water, being sufficient. Too strong an indicator gives confusing shades of green in the end reaction.†

A low table, placed near a window, is most convenient for bichromate titrations. The bichromate solution stands on a shelf,

*Ore which must be fused before titration of iron, should be fused with sodium carbonate alone. KNO_3 is unnecessary, as a ferrous, not ferric solution is required. If KNO_3 has been used, and the fused mass dissolved by HCl , some platinum from the crucible will be dissolved; and will interfere with reduction by SnCl_2 . HNO_3 from the KNO_3 will also interfere with the titration.

†If the analyst is at all color blind and finds the end reaction of the bichromate titration hard to strike, the modification used by Mr. L. R. Lenox, chemist of the U. S. Navy, at Washington, D. C., will be appreciated. The hollows of a spotting plate are filled with a very strong solution of ferricyanide, and the iron solution is diluted only to 150 cc. A drop of this let fall into the ferricyanide gives a heavy blue precipitate, changing to deep green color as more $\text{K}_2\text{Cr}_2\text{O}_7$ is added; and as the end reaction is reached giving place to a clear orange or brownish yellow. The end is unmistakable. Duplicate titrations are always made, the first to give the approximate per cent. The $\text{K}_2\text{Cr}_2\text{O}_7$ should always be standardized in the same manner as the titration is conducted.

and connects by a siphon with the bichromate burette. A flexible rubber tube, leading to the solution bottle, allows the operator to refill the burette without removing it from the stand. The operator can remain seated during the titration, and the labor of a number of iron determinations is thus reduced to a minimum.

The $K_2Cr_2O_7$ solution required is 4.392 gms. to a liter. One cc. of this is equal to .005 gm. iron ; or, if .5 gm. be taken, each cc. is equal to 1 per cent. iron in the ore.

In standardizing solutions, the same time should be given for the blue end reaction to appear, as is given in analysis of ores. A wire much purer than piano-forte wire can be obtained from Sargent & Co., of Chicago. This may be considered as pure Fe, and should be cut into pieces weighing approximately .300 gms. These can be kept free from rust by keeping a fragment of $CaCl_2$, wrapped in paper, in the glass stoppered bottle containing the wire.

Perhaps the shortest method for determination of iron in ores, but one in which the "personal equation," or liability of the analyst to err is a potent factor, is as follows: Dissolve half a gm. of fine ore in 15 cc. of strong HCl , reduce with $SnCl_2$, and add $HgCl_2$ to take up excess of reducing agent. Dilute to 400 cc., add 3 or 4 cc. H_2SO_4 , and titrate rapidly with $KMnO_4$ solution till a faint pink tint is obtained.

In determinations of silica in ores or slags, it is well to caution the beginner against the use of strong HCl to redissolve the residue after evaporation to dryness. The strong acid is apt to gelatinize silica ; and for this reason dilute hydrochloric, one part to three of water, should be used. This should be mixed before addition to the residue, since if strong acid be added, and then water to dilute, some silica is gelatinized.

Some analysts make very frequent use of a fusing mixture of K_2CO_3 , Na_2CO_3 , and KNO_3 , in treatment of insoluble residue. In most cases pure dry sodium carbonate serves as well, and, on account of the common use of dilute HCl to dissolve the fused mass in the crucible, the soda is safest to use. Hydrochloric acid generates chlorine, which attacks the crucible, if used to dissolve a fusion made with KNO_3 .*

*Fusion with KNO_3 in the mixture is almost always detrimental to the crucible. It should not be used in any case where Na_2CO_3 alone will do as well. Amateurs are very liable to use too much Na_2CO_3 , thereby loading the solution with alkaline salts, and necessitating very prolonged washing of precipitates.

Silica, burned without extra precautions, is apt to be carried from the crucible by the flame of the paper, or by the draft of the gasoline flame. In such ignitions as silica and graphite from pig iron, and silica in slags, the safest procedure is to place the paper and precipitate, still damp from the filtering flask, in the platinum crucible. This is placed about four inches above the gasoline burner; the point of a low flame being allowed barely to touch the bottom or side of the covered crucible. In a few minutes a smoke appears, which should not be allowed to ignite. When no further smoke issues, the crucible is uncovered, and the paper is found to be entirely charred, but still wrapped around and protecting the silica. The crucible is now placed directly on the burner, in a platinum triangle; turned on its side, the lid arranged to prevent a draft but allow circulation of air, and, at a low heat, the filter paper burned to an ash. With pig irons containing one per cent. of silicon and lower, the residue is sometimes very hard, and difficult to burn. This can be remedied by placing the crucible to cool on an iron slab, and crushing the residue in the crucible by a heavy glass rod. A miniature pestle, made by heating the end of a glass rod, and flattening it into a little disc on a smooth cold surface, is very convenient for this purpose. High silicon irons, ores and slags, do not require such treatment. The glass rod is examined to see that no silica or carbon clings to the disc, and the silica is ignited at a high heat till perfectly white.

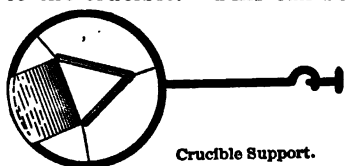
Certain foundry irons, known as softeners, carry a very high percentage of silicon. In certain cases the percentage of silicon is so high as to render the iron insoluble in acids. Mr. Williams* suggests that in such cases the drillings can be rendered soluble by fusion with sodium carbonate. In a large platinum crucible about 10 gms. Na_2CO_3 is fused and cooled. On this the drillings are thrown, more soda added, and the whole fused slowly for 20 minutes. An escape of carbon monoxide is noted, due both to reduction of sodium carbonate and partial oxidation of graphite. When this ceases, the mass is cooled and dissolved in HCl . All the silicon has united with soda as silicate. The solution is evaporated to dryness and silicon determined as usual.

This process of "smoking off" the filter paper is applicable to

*Trans. Am. Inst. Min. Eng. Vol., XVII, p. 542.

almost all precipitates, except such as contain oxides of metals liable to reduction by carbon. Filter paper, charred at a low heat, burns much more easily to ash than that ignited at once at a higher temperature.

To support crucibles over a Dangler lamp, it is very convenient to have two platinum triangles attached to rings over the burner. The cast iron star, or grating, supplied with these lamps is taken off; and two rings are attached to the support, one directly on the burner; the other, four or five inches above it. A platinum triangle attached to the upper ring, serves for "smoking off" the filter paper, while an ignition to whiteness may be carried on on the lower ring. The platinum wires supplied in these triangles are, as a rule, so light that at a very high heat they partially weld to the crucible. This can be remedied by wrapping the wires in



a strip of platinum foil, which keeps them cool. A wider strip of foil, wrapped around one wire and extending to the surrounding iron ring, forms a good support for the lid

when the crucible is laid on its side.

For rapid determinations of phosphorus at mines and rolling mills, Emmerton's titration method has been generally used. By this method underground samples at the mines can be quickly checked; and steel in the rolling mills can be examined with dispatch. As a court of final resort, however, where accuracy is above all things the point in question, no method has superseded the gravimetric magnesia method.

It is well to determine in every ore whether the phosphorus therein is entirely soluble in hydrochloric acid. In certain cases, notably some ores from the Lake Angeline mines,* about forty per cent. of the phosphorus remains insoluble. Such ores, of course, require fusion. In certain magnetites again, as those of the Lake Champlain region, all the phosphorus exists in combination with lime; and nitric acid will extract the phosphorus without the solution of much iron. This is also the case with a large number of Lake Superior hematites. In such cases the

*Mr. Bradt, Chemist of Lake Angeline mine, says that by grinding the ore much finer than is usually done, the phosphorus can be got entirely into solution in HCl.

method suggested by Mr. E. P. Jennings,* can be applied. A slight modification of his method is as follows: Five gms. of finely powdered ore are heated to boiling for half an hour with 50 cc. of dilute, (1-4), nitric acid. The undecomposed ore is filtered off, the filtrate treated with NH_4OH and HNO_3 , and phosphorus determined by the molybdate method.†

A rapid modification of Emmerton's process suggested by Clemens Jones‡ is as follows: The ore is dissolved in hydrochloric acid and filtered. The residue is fused with Na_2CO_3 , and dissolved in dilute H_2SO_4 . The filtrate is evaporated with HNO_3 , till chlorine is driven off. The solution of fused residue is added; and the iron is precipitated by NH_4OH . HNO_3 is added to re-dissolve and the phosphorus precipitated and titrated as usual.

In applying Emmerton's method to pig iron and steel, Mr. Porter W. Shimer suggests dissolving the metal in HNO_3 , and adding KMnO_4 solution after short boiling. This oxidizes any organic matter. The manganese precipitated is dissolved by adding a few grains of ferrous or ammonio ferrous sulphate. The solution is at once filtered, and phosphorus precipitated as before mentioned.

All these are but modifications of Emmerton's method as described in *Trans. Inst. Min. Eng.*, Vol. XV, p. 93.§ By the original method phosphorus can be determined in pig irons, with accuracy, sufficient for all commercial requirements, in two or three hours after the sample is weighed.

Mr. Clemens Jones suggests the use of dilute H_2SO_4 , 1-50, as wash water for the yellow precipitate instead of dilute nitric acid. The suggestion is a valuable one; inasmuch as the nitric wash water, adhering to funnels, is liable to destroy the accuracy of permanganate titrations. It is well to remember that, by this method, phosphorus is determined indirectly from the amount of molybdenum contained in the yellow precipitate. As this is a variable quantity, dependent upon the temperature and time of precipitation, it is most important that the same conditions should obtain in each analysis. The temperature should be

**Eng. Min. Jour.*, June 13, '85. *This Journal* 2, 90.

†*See Trans. Am. Inst. Min. Eng.* Vol. XVII, p. 752.

‡*Trans. Inst. Min. Eng.*, Feb. 1890, Washington meeting. *This Journal* 4, 268.

§*This Journal* 1, 93.

always 85°C. , and the same amount, 40 cc., of molybdate solution should in every case be used. In the analysis of high phosphorus ores, after filtering off the yellow precipitate, it is well to add a few cc. of molybdate solution to the filtrate, and allow it to stand a while, lest the percentage of phosphorus in the ore should have been above the precipitating power of 40 cc. of molybdate previously added. For Bessemer ores and irons 5 gms. of sample are generally used, while for foundry irons running .5 to .1 per cent. phosphorus, 1 gm. is sufficient.

The final reduction with zinc should be carried on for not less than ten minutes, and the solution should have an olive green tint, best seen in the bubbles on the surface, when ready to filter. In high phosphorus determination, reduction to this color is difficult; but persistent and violent boiling, with the addition from time to time of a little zinc dust, will effect the desired result. If the reduction is carried too far, crystals of zinc sulphate will precipitate. If this occurs, a liberal amount of boiling water should be added to the solution.

Phosphorus precipitated by standing at a moderate heat over night, can not be filtered by pressure, like that precipitated by shaking. The former is too finely divided, and passes through the pores of the paper.

Zinc used for reduction need not necessarily be chemically pure, since the only essential requirement is that it be free from iron, or other oxidizable element, which would interfere with KMnO_4 titration. This should be flaked before using. To do this satisfactorily, it is necessary that the zinc should be melted, at as low a heat as possible, in a Battersea crucible. Zinc will burn to oxide if a high heat is used. The crucible is taken off the forge fire, skimmed with a bit of wood, and allowed to cool till it no longer ignites a stick thrust into the molten metal. Then, by grasping with a blacksmith's tongs, the metal can be poured, drop by drop, from a height of about six feet, into a bucket of water. Pouring when very hot causes the zinc to assume the form of drops or shot, which are not of so much use in rapid reductions. Five or ten gms. of this flaked zinc should be dissolved in dilute H_2SO_4 , and KMnO_4 added till a pink color is obtained to

get the correction for the zinc. In the case of good zinc a drop or two is all that will be required.

In determinations of phosphorus by the gravimetric magnesia method, some chemists, following the directions given by Fresenius, Quant. Anal. p. 743, ed. of '82, omit to remove silica from the yellow precipitate before reprecipitating by magnesia. This precaution is very necessary. After dissolving the yellow precipitate in NH_4OH , addition of strong HCl is made till the solution is almost neutral, and has a peculiar and rather pleasant odor. A slight milkiness is now generally perceived in the solution. The beaker should be covered with a glass and placed upon the steam pipes until silica, as a flaky, white precipitate, settles down. This is filtered off, and magnesia mixture added.

As magnesia mixture contains alkaline ammonium chloride, it is liable to attack the bottle containing it, and cause the glass to scale or peel off. For this reason, as well as to ensure slow addition of the magnesia* to the phosphorus solution, the magnesia mixture should be poured upon a filter paper under which the solution of the yellow precipitate, to which a third of its volume of ammonia has been added, is placed. As the magnesia passes through the paper the solution should be stirred with a small glass rod. The sides of the beaker should not be touched by the rod in stirring, as this will cause the precipitate of magnesium ammonium phosphate to adhere very closely to the glass where the beaker was touched by the rod.

After the magnesia phosphate has stood some time, preferably over night, it is filtered, washed, ignited, and weighed; while the filtrate from the magnesia precipitate, containing of course all the molybdenum previously combined with phosphorus in the yellow precipitate, can be reduced with zinc and H_2SO_4 and titrated by KMnO_4 . This furnishes a check in case the magnesia precipitate should be lost before weighing or the results might seem open to suspicion.

A table giving the percentage of phosphorus in any given weight of magnesia phosphate obtained from five gms. of ore or metal, should hang near the balance case. A similar table, giving the percentage of silicon, calculated from the amount of silica

*Crookes' Select Methods, Chem. Anal., 2d ed. p. 519.

obtained from 1 gm. of metal, will save much calculation. Such tables will be found at the end of this article.

At some rolling mills it is customary to analyze each cast of iron made at the furnaces for sulphur. In this case rapidity of work is important, since the molten metal is often taken in buggies or ladles directly from the furnace to the converter, and it is important that sulphur in the finished product be kept below a stated amount. For rapid determination of sulphur, the potash absorption and iodine titration method is perhaps the most satisfactory.* Some precautions must be observed in carrying out the process. The caustic potash, a very good substitute for caustic soda, used, should be free from sulphur. A solution of 1 part of stick potash to 5 of water is generally used. The rubber stoppers used in flasks or test tubes containing KOH are to be previously boiled in potash to remove adhering sulphur. The titration with iodine, if a few drops only of starch solution be used as indicator, has a rather vague and unsatisfactory end reaction. A more decisive reaction could be obtained by adding 3 or 4 cc. starch solution, instead of three or four drops. The dense opaque blue, and not the first transparent tint is to be taken as the final point or end reaction. The titrations should be carried on very rapidly, since H_2S is liable to escape after acidulation of the KOH solution. The iron drillings used should not be placed in the flask before the analysis is about to commence. Otherwise they may be oxidized by some moisture in the flask, and in this way some sulphur be changed to sulphate, and escape the final determination.

Much more accurate, where small amounts of sulphur exist in pig iron, is the process of oxidation to H_2SO_4 by permanganate, known as Drown's† method.

Volhard's‡ method is probably the most rapid method for determination of manganese in iron and steel. The difficulty of striking an undoubted end reaction in this method renders it somewhat unsatisfactory to the amateur. A good deal of trouble in distinguishing between the brown coloration of floating MnO_2 and the pink tint of $KMnO_4$ may be avoided by having the solution

*Chem. News, XXIII, 61; also Blair Anal. of Iron, p. 60.

†Trans. Inst. Min. Eng. II, 224.

‡Blair Chem. Anal. of Iron, p. 98. Trans. Inst. Min. Eng. X, 204.

almost boiling while titrating with permanganate, and, after each addition, shaking to precipitate the manganese. The color can be readily seen by turning the flask on one side; so as to bring the liquid above the level of manganese discoloration of glass, and looking through the liquid to a white-washed wall or sheet of paper.

Williams'* method is, except in point of rapidity, much more satisfactory. A few precautions must be mentioned. The nitric acid used for washing the precipitated MnO_2 ,† must be free from yellow color; as the nitrous fumes, to which this color is due, cause reduction and resolution of this precipitate. The precipitate, after washing with HNO_3 , must be sucked dry, and the HNO_3 in the filtering flask removed before washing with cold water. This is necessary, since dilute nitric acid is capable of dissolving the manganese precipitate; and any manganese dioxide, carried by accident through the asbestos filter, would dissolve in the mixture of nitric acid and water in the flask below. If the nitric acid be first removed, the wash water can be refiltered and MnO_2 recovered.

Short-fibered asbestos, general opinion to the contrary notwithstanding, makes a closer and quicker filter than long-fibered. The best way to form a good asbestos filter is to place a "carbon funnel" in the filtering flask. In this a small piece of platinum foil perforated and pressed out like a dish is placed. A few gms. of short-fibered, clean asbestos are stirred up with about 50 cc. of water, and the liquid poured, without pressure, upon the carbon funnel. A few repetitions of this forms a soft precipitate of asbestos in the tube. This is compacted by suction and made even with the point of a glass rod.

After the manganese dioxide has been washed free from nitric acid, it is placed in a flask, and the requisite amount of ferrous sulphate or oxalic acid for reduction added. A little clean lake or sea sand,‡ previously freed from iron by heating with HCl , may now be added, and the flask corked and shaken. The sand breaks up the packed asbestos and manganese, and causes ready solution in the reducing agent. Titration is then made with

*Trans. Inst. Min. Eng. X, 100.

†See Trans. Inst. Min. Eng. IX, 397.

‡Mr. Emmerton's practice at Joliet Steel Works.

KMnO_4 , to find the amount of ferrous sulphate or oxalic acid left unoxidized.

A neat adaptation of Volhard's method to a gravimetric determination was first brought to my notice by Mr. W. S. McKeown, of Youngstown. A gm. of iron or steel is treated as for manganese by Volhard's method. (If 1.333 gm. be taken, calculations are much simpler.) The process is carried on till the zinc paste is added to the solution in a 300 cc. flask. Two hundred cc. of the filtrate from this are placed in a flask, heated and bromine added, but no ammonia is used lest some iron be precipitated. Manganese is precipitated by heat and further addition, if necessary, of bromine. The precipitate is filtered on a No. 589 filter, and poured off the paper into a small beaker. Dilute acetic acid is added and stirred around. The filtration is carried on, using dilute acetic acid to wash free from iron. The precipitate is very carefully ignited and calculated as Mn_2O_3 . Results seem to be accurate. If 1.333 gm. is used, and two-thirds of this taken by pipette, the resulting precipitate of Mn_2O_3 is calculated as coming from 1 gm. of iron.

Much of the difficulty which surrounds the gravimetric determination of carbon in steel and iron may be obviated by careful and intelligent preparation of the preliminaries. The apparatus described on page 337 should be kept in working order. All the rubber connections should be wound with thread or fine wire to ensure accuracy, and the corks protected by a liberal application of sealing wax. It is very necessary, when the apparatus is first set up, to pass a stream of CO_2 , generated in the flask *A*, by acid and limestone, through the tubes. The calcium chloride is apt to contain a little caustic lime, which, unless previously saturated with carbon dioxide, would interfere with the absorption of the gas in the potash tubes alone.

After the apparatus has been placed in position, and the carbonaceous or graphitic residue, obtained from the iron, washed free from all foreign elements, the asbestos filter and residue are placed in the flask *A*, with as little water as possible. Not over 10 cc. should be used. Small pieces of moist asbestos held in pincers are used to wipe out the carbon funnel; and these with the residue are transferred to the flask. About 100 cc. strong H_2SO_4 is

then added to the flask, care being taken to add the acid slowly, and avoid spitting or bumping of the solution from the ensuing heat. The flask is cooled till it reaches the temperature of the room, 10 gms. of CrO_3 are added,* and the flask fastened to the apparatus. About a liter of air is drawn through the entire apparatus and potash bulbs, in order that no atmospheric carbon dioxide may remain in the flask or tubes. The potash bulbs and calcium chloride tubes are now weighed, replaced, and a lamp, turned very low, set under the flask *A*. This is very gradually heated to boiling, care being taken to lower the heat if bubbles pass faster than three or four per second. When no further gas passes over, shake the flask *A* with a rinsing motion to get down any carbon clinging to the sides. Do not allow the tube *O* to become heated as far as the condenser. Lower the light gradually; attach tube *P* to the aspirator *J*. Start a gradual stream of water by opening the pinch-cock *Q* very slightly with a match or tooth pick, open the stopcock *M* which has been closed during combustion, and draw a liter or two of air through. Detach bulbs and weigh. Instead of the shelf *G*, a small box nailed to the support forms a very convenient receptacle for the absorption apparatus. It is very important that all the hydrochloric acid and chlorides should have been removed from the carbonaceous residue before it is placed in the oxidizing flask.† In order to make assurance doubly sure, some operators prefer to place a bulb containing a solution of silver nitrate between the first tube containing H_2SO_4 and the second containing CaCl_2 .

Passing now to the analysis of slags, the determinations which most frequently engage the analyst's attention, are those of silica, alumina and lime. An occasional complete analysis may be required; but as a rule, the working of a furnace can be determined by the amounts of these elements present in the slag.

Fusion of a blast furnace slag is not always necessary,‡ and, on account of the large amount of alkaline salts it introduces into the analysis, it should be dispensed with wherever possible. Some blast furnace slags, particularly those made with hot foundry irons, are soluble in dilute hydrochloric acid. Slags containing

*Mr. Emmerton's practice at Joliet Steel Works.

†See this Journal 5, 129.

‡Fusion is not as often required as might be thought necessary. Solution should always be tried where the oxygen is much below bisilicate in slags.

about 30 per cent. SiO_2 , with about 45 per cent. lime are thus readily soluble. Analysis for silica without fusion can more readily be made if the slag has been chilled when taken. The process of analysis is as follows: One gm. of finely powdered sample is taken in an 8 oz. beaker, water enough to suspend the particles is added with shaking, strong hydrochloric acid added slowly, the beaker warmed a short time, when the solution is found clear. This is evaporated to dryness, baked, redissolved in *dilute* HCl , filtered, washed with hot dilute HCl and hot water, ignited and weighed. If sufficient strong HCl be added to the slag at once, without addition of water to suspend the particles, it causes gelatinization of silica, which covers some undissolved slag and prevents further action of the acid.* If the resulting silica is perfectly white, as is generally the case, and if the percentage is the same as that obtained by the ordinary fusion method, there is no necessity for further fusions of similar slags. The same precautions as to the use of dilute hydrochloric acid to redissolve the silica after evaporation to dryness, should be observed as are necessary in the case of ores.

The filtrate for silica should be taken in a 20 oz. beaker, and iron and alumina thrown down either by ammonia or the basic acetate method. If the manganese is to be determined the latter method must be employed, but where this is not necessary ammonia is more simple and rapid. The boiling filtrate is precipitated by careful addition of NH_4OH , and filtered after settling on a $12\frac{1}{2}$ cm. filter paper, No. 597. If the filtration is a trifle slow, it may be hastened by lengthening the stem of the funnel by attaching a short piece of glass tubing. If, however, the solution was boiling before ammonia was added, and if only slight excess of alkali was used, and the solution again brought to the boil for just a moment, the filtration with this make of paper will be quite rapid. After the precipitate has been washed a couple of times, the funnel is taken from the support, held horizontally over the beaker in which precipitation was made and by the aid of a wash bottle of hot water the precipitate is rinsed out into the beaker. The funnel is now replaced in the support, and what little precipitate remains, is removed by washing with hot dilute HCl . The acid

*Mr. G. W. Whyte, private communication.

running through into the beaker below will readily dissolve the precipitate. By this means the troublesome solution on the filter with acid is done away with, as well as the equally tedious expedient of digging out the iron and alumina with a spatula. Very little water is needed to get the precipitate into the beaker, and an excess of acid need not be used to get it in solution. This is reprecipitated as before, and thoroughly washed with hot water. The precipitate should be dried in the funnel, and the paper ignited separately.* The iron and alumina should be ignited at a very low red heat until the particles look dark and glassy at the edges. Unless all the ammonium chloride has been removed from the precipitate by thorough washing white fumes may be seen during ignition, and volatilized chloride of iron will be absorbed by the platinum crucible, forming a coating difficult to clean except by fusion with KHSO_4 and reduction with Zn and strong HCl.

The united filtrates from alumina and iron require in some cases to be concentrated before precipitation of lime. The oxalate of lime precipitate should in every case be redissolved and reprecipitated to free from any magnesium oxalate. Ignition of calcium oxalate for twenty minutes at the highest heat of the blast lamp serves to dispel all CO_2 , and no appreciable change in weight of the precipitate will be noticed after ignition for that length of time.†

Where a small amount of iron is to be determined in a slag it is necessary to remove silica before titration. It is very difficult to determine iron in a solution containing a large amount of silica, as the end reactions are very slow. The silica seems to retain part of the iron and prevents thorough oxidation. It must be remembered that iron as a rule exists in furnace and foundry slags as ferrous silicate, and hence should be calculated and reported as FeO . In the alumina and iron precipitate, however, it exists as ferric oxide, and in order to obtain the amount of alumina, the iron obtained by titration should be calculated to ferric oxide, and subtracted from the weight of iron and alumina precipitate.

*A small bench, fitted with holes like a funnel support, and holding several broken funnels, is a very convenient arrangement for holding precipitates to dry in the drying oven, or over steam pipes.

†If MgO is to be determined, it is better to prepare fresh $(\text{NH}_4)_2\text{C}_2\text{O}_4$ for the precipitation of CaC_2O_4 . A solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, if kept any length of time, is liable to attack the glass bottle and extract magnesia salts which would vitiate the results.

The determination of manganese in slags and ores, where the basic acetate separation is made, while not essentially difficult, is on account of the precautions necessary, one of the most troublesome of the more common analyses. For a summary of the cautions necessary in this method, the reader is referred to Blair's Analysis of Iron, page 93. Much of the difficulty experienced in making this analysis may be avoided by reducing the method to a routine. The short summary of the method here given will be found reliable. The concentrated (50 cc.) solution in HCl (no HNO_3 should be present) is exactly neutralized by Na_2CO_3 in a two liter flask. Solution should be very dark, but clear. Ten cc. acetic acid are added and immediately 2 or 3 gms. of $\text{NaC}_2\text{H}_3\text{O}_2$ dropped in. About 400 cc. of boiling water is added and the flask kept boiling for about two minutes. The precipitate should be redissolved and reprecipitated. The united filtrates are concentrated to about 300 cc; about 10 gms. sodium acetate added to change manganous chloride to acetate, and bromine water added. The precipitate which settles out on heating may be filtered and weighed as Mn_2O_3 , or it may be dissolved in H_2SO_4 and reprecipitated as phosphate if great accuracy is desired. Many analysts claim that if the MnO_2 precipitate be burned at a low and even heat and calculated as Mn_2O_3 , the results are as accurate as those obtained by precipitation as phosphate.

Of the determination of such substances as copper in steel and titanium and tungsten in ores, nothing need herein be said. Of these analyses the text-books furnish ample detail. It is only concerning the more common analyses that the aim of the author has been to recapitulate certain precautions and details, which from their very simplicity and apparent obviousness are apt to be overlooked both by teacher and text-book.*

*The accuracy of a result is not always determined by the sum of 100 for the percentages found; in fact such an even addition of the constituents always gives rise to a suspicion that the results have been "doctored," or that the errors have averaged to produce a total of 100. If the number 100 represents the sample taken, the sum total may, without question of accuracy, be more or less than this. The many operations unavoidably occasion loss, either by incomplete precipitation, or by partial solution of precipitates in wash water; but these losses are in a measure balanced by co-precipitation of other constituents than those it is sought to precipitate. Unavoidable loss would cause the sum of results to be less than 100. An excess over 100 may result from imperfect washing of precipitates, or from calculating on an incorrect basis, the results obtained. Thus: Iron in slag may be determined correctly, but it may be calculated to exist as FeO or Fe_2O_3 , when in reality it may exist as finely divided metallic iron. This calculation as oxide would cause a sum of results greater than 100. Of two methods which seem equally correct, that one should be selected in which the substance to be found forms the smallest percentage of the precipitate in which it is weighed. This reduces the liability of error to a minimum.

The following tables of percentages of silicon and phosphorus in weighed quantities of silica and pyrophosphate of magnesia as well as the condensed statements of empirical solutions required in the analyses herein mentioned will, it is hoped, prove valuable. The tables for silicon and phosphorus, in 1 and 5 gm. samples—the amounts usually taken,—may have been published before, but the author has been unable to find them in any text-book in the form here given.

“Patience, cleanliness, and a firm reliance on the immutability of the laws of nature, are indispensable to success in chemical manipulation.”

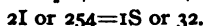
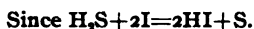
EMPIRICAL SOLUTIONS.

Iron Titration.— $K_2Cr_2O_7$. Take 4.392 gms. to the liter. 1 cc. solution = .005 gm. iron, or if .5 gm. ore be taken each cc. = 1 per cent. iron.

$SnCl_2$. 50 gms. in 500 cc. boiling dilute (1-1) HCl. Add 5 gms. metallic tin and keep tin in bottom of bottle.

$HgCl_2$. A saturated solution.

Sulphur Titration.—Iodine solution. 5 gms. iodine and 7 gms. KI dissolved in 20 cc. H_2O . When dissolved, *but not before*, water is added to make 1 liter. This is standardized so that 1 cc. contains .00397 gm. iodine.



Hence .00397 gm. I = .0005 sulphur, and 5 gms. being taken, 1 cc. I = .05 per cent. S.

To standardize iodine solution. Make up hyposulphite soda solution. 25 gms. $Na_2S_2O_3$ in 1 liter H_2O . Use same bichromate solution as for iron, 4.392 gms. to liter. 1 cc. = .011337 iodine.

To standardize iodine. Dissolve 1 gm. KI in 15 cc. H_2O ; add 20 cc. $K_2Cr_2O_7$ and 20 cc. HCl (1-1) = .22647 iodine set free. Find how many cc. $Na_2S_2O_3$ solution neutralize this and calculate strength $Na_2S_2O_3$ in terms of iodine. Take then 20 cc. iodine solution and add hyposulphite solution till neutralized and no iodine color left. Calculate then how much I in 1 cc. iodine solution. Make iodine solution of such strength that 1 cc. = .00397 gm. I = .0005 gm. sulphur equals .01% sulphur if 5 gms. sample were used.

Phosphorus Titration. Take 3.472 gms. $KMnO_4$ to 1 liter H_2O , (do not dissolve in hot water). Take 1.4 gm. pure ammonium ferrous sulphate (= .200 gm. iron), dissolve in H_2O and 2 cc. H_2SO_4 . Titrate with $KMnO_4$. When of correct strength should require 32.5 cc. solution to give color. 1 cc.

KMnO₄ should equal .006153 gm. iron, in order that 1 cc. should be equivalent to .0001 gm. phosphorus. With this strength, if 1 gm. sample be taken, each cc. KMnO₄ required to oxidize the molybdate reduction is equivalent to .01 per cent. phosphorus.

Manganese Titration. Volhard's method. 1 gm. sample taken and two-thirds or .666 gm. sample being treated with KMnO₄ solution. The KMnO₄ should be 1.27 gm. to liter, 1 cc. should equal .002262 gm. iron. Hence .7 gm. pure ammonium ferrous sulphate (.1 gm. Fe) should require 44.20 KMnO₄ solution.

One cc. of such solution equals .000666 gm. manganese in the metal or .10 per cent. Mn if 1 gm. be taken for analysis.

Manganese Titration. By Williams' method. For Pig Iron. Take 14 gms. ammonium ferrous sulphate in 900 cc. H₂O and 100 cc. H₂SO₄, dilute or add more iron till of such strength that 1 cc.=.002 gm. iron. Add 100 cc. to the MnO₂ precipitated by HNO₃ and KClO₃. Use KMnO₄ as for phosphorus 1 cc.=.006153 gm. iron=.003021 gm. Mn. 100 cc. of ammonium ferrous sulphate solution=.2 gm. iron=32.5 cc. KMnO₄. If, say 12.5 cc. KMnO₄ required to oxidize iron solution, after the action of MnO₂, then 32.5-12.5=20 cc. KMnO₄ are the equivalent of the MnO₂ in oxidizing power. 20 cc. KMnO₄ (20×.003021)=.06042 gm. manganese in the sample.

For Spiegel and Ferro-Manganese a very strong iron solution is required; 50 gms. FeSO₄ to liter.

Calculation of Silicon in percentages from the Silica resulting from one gram of Iron.

Weight in gms. SiO ₂ .	Per Cent. Si.	Weight in SiO ₂ .	Per Cent. Si.	Weight in gms. SiO ₂ .	er Cent. Si.	Weight in gms. SiO ₂ .	Per Ct. Si.
.0002	.01	.0040	.19	.0078	.37	.0117	.55
.0004	.02	.0042	.20	.0080	.38	.0119	.56
.0006	.03	.0044	.21	.0082	.39	.0121	.57
.0008	.04	.0046	.22	.0085	.40	.0123	.58
.0010	.05	.0049	.23	.0087	.41	.0125	.59
.0012	.06	.0051	.24	.0089	.42	.0128	.60
.0014	.07	.0053	.25	.0092	.43	.0130	.61
.0016	.08	.0055	.26	.0094	.44	.0132	.62
.0018	.09	.0057	.27	.0096	.45	.0135	.63
.0021	.10	.0059	.28	.0098	.46	.0137	.64
.0023	.11	.0061	.29	.0100	.47	.0139	.65
.0025	.12	.0063	.30	.0102	.48	.0141	.66
.0028	.13	.0065	.31	.0104	.49	.0143	.67
.0030	.14	.0067	.32	.0107	.50	.0145	.68
.0032	.15	.0070	.33	.0109	.51	.0147	.69
.0034	.16	.0072	.34	.0111	.52	.0150	.70
.0036	.17	.0074	.35	.0113	.53	.0152	.71
.0038	.18	.0076	.36	.0115	.54	.0154	.72

Weight in gms. SiO ₂ .	Per Cent. Si.	Weight in gms. SiO ₂ .	Per Cent. Si.	Weight in gms. SiO ₂ .	Per Cent. Si.	Weight in gms. SiO ₂ .	Per Ct. Si.
.0157	.73	.0325	1.52	.0552	2.58	.0780	3.64
.0159	.74	.0330	1.54	.0557	2.60	.0784	3.66
.0161	.75	.0334	1.56	.0591	2.62	.0788	3.68
.0163	.76	.0338	1.58	.0565	2.64	.0792	3.70
.0165	.77	.0342	1.60	.0570	2.66	.0797	3.72
.0167	.78	.0347	1.62	.0574	2.68	.0801	3.74
.0169	.79	.0351	1.64	.0578	2.70	.0805	3.76
.0171	.80	.0355	1.66	.0582	2.72	.0810	2.78
.0173	.81	.0360	1.68	.0587	2.74	.0814	3.80
.0175	.82	.0364	1.70	.0591	2.76	.0818	3.82
.0178	.83	.0368	1.72	.0595	2.78	.0822	3.84
.0180	.84	.0372	1.74	.0600	2.80	.0827	3.86
.0182	.85	.0377	1.76	.0604	2.82	.0831	3.88
.0184	.86	.0381	1.78	.0608	2.84	.0835	3.90
.0186	.87	.0385	1.80	.0612	2.86	.0840	3.92
.0188	.88	.0390	1.82	.0617	2.88	.0844	3.94
.0190	.89	.0394	1.84	.0621	2.90	.0848	3.96
.0192	.90	.0398	1.86	.0625	2.92	.0852	3.98
.0194	.91	.0402	1.88	.0630	2.94	.0857	4.00
.0196	.92	.0407	1.90	.0634	2.96	.0861	4.02
.0199	.93	.0411	1.92	.0638	2.98	.0865	4.04
.0201	.94	.0415	1.94	.0642	3.00	.0870	4.06
.0203	.95	.0420	1.96	.0647	3.02	.0874	4.08
.0205	.96	.0424	1.98	.0651	3.04	.0878	4.10
.0207	.97	.0428	2.00	.0655	3.06	.0882	4.12
.0209	.98	.0432	2.02	.0660	3.08	.0887	4.14
.0211	.99	.0437	2.04	.0664	3.10	.0891	4.16
.0214	1.00	.0441	2.06	.0668	3.12	.0895	4.18
.0219	1.02	.0445	2.08	.0672	3.14	.0900	4.20
.0223	1.04	.0450	2.10	.0679	3.16	.0904	4.22
.0228	1.06	.0454	2.12	.0681	3.18	.0908	4.24
.0232	1.08	.0458	2.14	.0685	3.20	.0912	4.26
.0236	1.10	.0462	2.16	.0690	3.22	.0917	4.28
.0242	1.12	.0467	2.18	.0694	3.24	.0921	4.30
.0244	1.14	.0471	2.20	.0698	3.26	.0925	4.32
.0248	1.16	.0475	2.22	.0702	3.28	.0930	4.34
.0252	1.18	.0480	2.24	.0707	3.30	.0934	4.36
.0257	1.20	.0484	2.26	.0711	3.32	.0938	4.38
.0261	1.22	.0488	2.28	.0715	3.34	.0942	4.40
.0265	1.24	.0492	2.30	.0720	3.36	.0947	4.42
.0270	1.26	.0497	2.32	.0724	3.38	.0951	4.44
.0274	1.28	.0501	2.34	.0728	3.40	.0955	4.46
.0278	1.30	.0505	2.36	.0732	3.42	.0960	4.48
.0282	1.32	.0510	2.38	.0737	3.44	.0964	4.50
.0287	1.34	.0514	2.40	.0741	3.46	.0968	4.52
.0291	1.36	.0518	2.42	.0745	3.48	.0972	4.54
.0295	1.38	.0522	2.44	.0750	3.50	.0977	4.56
.0300	1.40	.0527	2.46	.0754	3.52	.0981	4.58
.0304	1.42	.0531	2.48	.0758	3.54	.0985	4.60
.0308	1.44	.0535	2.50	.0762	3.56	.0990	4.62
.0312	1.46	.0540	2.52	.0767	3.58	.0994	4.64
.0317	1.48	.0544	2.54	.0771	3.60	.0998	4.66
.0321	1.50	.0548	2.56	.0775	3.62		

Calculation of percentage of Phosphorus in $Mg_3P_2O_7$ from 5 grams sample taken. For Bessemer Ores, Iron and Steel.

Wt. in gms. $Mg_3P_2O_7$.	Per Cent. P.	Wt. in gms. $Mg_3P_2O_7$.	Per Cent. P.	Wt. in gms. $Mg_3P_2O_7$.	Per Cent. P.	Wt. in gms. $Mg_3P_2O_7$.	Per Cent. P.
.0001	.00056	.0051	.0285	.0101	.0565	.0151	.0844
.0002	.00122	.0052	.0291	.0102	.0570	.0152	.0850
.0003	.00168	.0053	.0296	.0103	.0576	.0153	.0855
.0004	.00224	.0054	.0302	.0104	.0581	.0154	.0861
.0005	.0028	.0055	.0307	.0105	.0587	.0155	.0867
.0006	.0033	.0056	.0313	.0106	.0592	.0156	.0872
.0007	.0039	.0057	.0318	.0107	.0598	.0157	.0877
.0008	.0045	.0058	.0324	.0108	.0604	.0158	.0883
.0009	.0050	.0059	.0329	.0109	.0609	.0159	.0888
.0010	.0056	.0060	.0335	.0110	.0615	.0160	.0894
.0011	.0061	.0061	.0340	.0111	.0620	.0161	.0899
.0012	.0067	.0062	.0346	.0112	.0626	.0162	.0905
.0013	.0072	.0063	.0351	.0113	.0632	.0163	.0911
.0014	.0078	.0064	.0357	.0114	.0637	.0164	.0917
.0015	.0084	.0065	.0363	.0115	.0643	.0165	.0922
.0016	.0089	.0066	.0369	.0116	.0648	.0166	.0928
.0017	.0095	.0067	.0374	.0117	.0654	.0167	.0934
.0018	.0101	.0068	.0380	.0118	.0660	.0168	.0939
.0019	.0106	.0069	.0385	.0119	.0666	.0169	.0945
.0020	.0112	.0070	.0391	.0120	.0671	.0170	.0950
.0021	.0117	.0071	.0396	.0121	.0677	.0171	.0956
.0022	.0123	.0072	.0402	.0122	.0682	.0172	.0961
.0023	.0128	.0073	.0407	.0123	.0688	.0173	.0967
.0024	.0134	.0074	.0413	.0124	.0693	.0174	.0973
.0025	.0140	.0075	.0419	.0125	.0699	.0175	.0978
.0026	.0145	.0076	.0424	.0126	.0704	.0176	.0984
.0027	.0151	.0077	.0430	.0127	.0710	.0177	.0989
.0028	.0156	.0078	.0435	.0128	.0716	.0178	.0995
.0029	.0162	.0079	.0441	.0129	.0721	.0179	.1000
.0030	.0168	.0080	.0447	.0130	.0726	.0180	.1006
.0031	.0173	.0081	.0453	.0131	.0732	.0181	.1012
.0032	.0179	.0082	.0458	.0132	.0738	.0182	.1017
.0033	.0185	.0083	.0464	.0133	.0743	.0183	.1023
.0034	.0190	.0084	.0469	.0134	.0748	.0184	.1028
.0035	.0196	.0085	.0475	.0135	.0754	.0185	.1034
.0036	.0200	.0086	.0481	.0136	.0760	.0186	.1039
.0037	.0207	.0087	.0486	.0137	.0766	.0187	.1045
.0038	.0212	.0088	.0492	.0138	.0771	.0188	.1050
.0039	.0218	.0089	.0497	.0139	.0777	.0189	.1056
.0040	.0224	.0090	.0503	.0140	.0782	.0190	.1062
.0041	.0229	.0091	.0509	.0141	.0788	.0191	.1067
.0042	.0235	.0092	.0514	.0142	.0794	.0192	.1073
.0043	.0241	.0093	.0520	.0143	.0799	.0193	.1078
.0044	.0246	.0094	.0525	.0144	.0804	.0194	.1084
.0045	.0252	.0095	.0531	.0145	.0810	.0195	.1090
.0046	.0257	.0096	.0536	.0146	.0815	.0196	.1095
.0047	.0263	.0097	.0542	.0147	.0821	.0197	.1101
.0048	.0268	.0098	.0548	.0148	.0827	.0198	.1107
.0049	.0274	.0099	.0553	.0149	.0833	.0199	.1112
.0050	.0280	.0100	.0559	.0150	.0838	.0200	.1118

THE DETERMINATION OF ROSIN IN ITS MIXTURES WITH FATTY ACIDS.

BY E. TWITCHELL, SUPT. OF THE EMERY CANDLE CO., CINCINNATI, OHIO.

The ethyl ethers of fatty acids, as is well known, are most readily formed by acting on an alcoholic solution of the latter with hydrochloric acid gas, the HCl merely serving to remove the water formed by the combination. This reaction I have found to be practically complete where the alcohol employed is absolute, and the HCl gas is passed to saturation. No other precautions are necessary.

On attempting to etherify resin acids (common rosin) in the same way, I found that no combination takes place between the alcohol and acid, and that, when the solution is kept cool, the resin acid is entirely unacted on, and can again be separated by diluting with water and boiling to collect the precipitate.

This important difference suggested a method for separating rosin from fatty acids which, on being practically applied, gave me separations such as I think are impossible by any of the methods now in use.

The analysis may be either gravimetric or volumetric, and depends on the fact that, by the means indicated, all the fatty acids are combined to form ethers which are neutral in alcoholic solution and unacted upon by alkalies in the cold, while the rosin is left as it was, reacts acid in alcoholic solution with phenolphthaleine and combines easily with caustic potash to form a soluble soap. It is therefore simply necessary to effect the combination of the fatty acids with alcohol, when the resin acids may be titrated with standard NaOH solution, using phenolphthaleine as indicator, or they may be combined with KOH, and the rosin soap thus formed separated from the unsaponified fatty ethers by extracting with naphtha in a separatory funnel.

The gravimetric method is carried out as follows: 2 or 3 gms. of the mixture of fatty acid and rosin are dissolved in 10 times their volume of absolute alcohol in a flask, and dry HCl gas passed through in a moderate stream. The flask is set in a vessel with water to keep it cool. The HCl is rapidly absorbed, and, after about 45 minutes, the ethers separate, floating on the

solution, and no more HCl is absorbed. The flask is removed and allowed to stand a half hour longer to ensure a complete combination of the alcohol and fatty acid. It is then diluted with about five times its volume of water and boiled until the acid solution is clear, the ethers, with rosin in solution, floating on top. To this is added some naphtha and the whole transferred to a separatory funnel, the flask being washed out with naphtha. The acid solution is then run off and the naphtha solution (which ought to measure about 50 cc.) washed once with water and then treated in the funnel with a solution of .5 gm. KOH and 5 cc. alcohol in 50 cc. water and agitated. The rosin is immediately saponified and the two layers separate completely. The solution of rosin soap can then be run off, treated with acid, the rosin collected in any manner desired, dried and weighed. A second washing of the soap with naphtha is hardly necessary, as very little remains after the first extraction. The naphtha used is 74° gasoline, and for this purpose is much to be preferred to ether.

The first stages of the volumetric method are similar to those of the gravimetric, with the exception that the contents of the flask are washed into the separatory funnel with ether instead of naphtha, and the ether solution in the funnel is then thoroughly washed with water, until the wash water is no longer acid; 50 cc. alcohol, previously neutralized, are then added and the solution titrated with standard NaOH solution. If the combining equivalent of rosin is known, its percentage may be calculated, or some of the original mixture may be also titrated, when the difference in NaOH required will correspond to the fatty acids converted into ether.

I have tested this method by a number of experiments, some of which I will here describe. As a first step it was necessary to determine the effect of HCl gas on alcoholic solutions of fatty and of resin acids separately.

(1.) Five gms. of distilled fatty acids were dissolved in 50 cc. absolute alcohol, treated with HCl gas in the manner described, then treated with water, boiled, washed in a separatory funnel and dried. They yielded 5.451 gms. of ethyl ethers. These ethers were dissolved in neutralized alcohol and titrated with a normal solution of NaOH. They required for neutralization .14 cc. of

the solution. This would represent .97 per cent. of resin acid, taking 346 as the combining equivalent of rosin, i. e., the weight of rosin neutralized by 1 cc. normal alkali=.346 gms.

(2.) Five gms. fatty acids from a low grade tallow were treated in the same way, and required .06 cc. for neutralization=.41 per cent. rosin.

These figures, although not indicating a perfect combination, are still very small, and I think can be explained, especially in the first case, by the supposition that there were actually some resin acids present, natural constituents of the crude fats.

On attempting to use alcohol of 90 per cent. instead of the absolute, I could only succeed in etherifying 92 per cent. of the fatty acids.

(3.) Five gms. of an average sample of rosin were treated in exactly the same manner as in working with the fatty acids. After diluting with water and boiling, the rosin was collected by dissolving in a little ether and found to weigh 4.9382 gms. This was dissolved in alcohol and required 14.27 cc. of the NaOH solution to neutralize it. Five gms. of the original rosin were titrated and required 14.45 cc. There had been a slight loss in drying, but no change in the combining weight.

It was found that if the alcoholic solution became heated by the HCl gas, or if the solution was boiled without first diluting with water, the rosin suffered some change and required less NaOH to neutralize it.

Analyses were made of a number of mixtures. In using the volumetric method the mean combining weight of fatty acids was taken at 275 and of rosin, 346.

A mixture consisting of 20 per cent. rosin, 80 per cent. f. a. gave, by the volumetric method, 20.36 per cent., 21.40 per cent., and 19.91 per cent. rosin. The same, by the gravimetric method: 18.93 per cent. rosin.

A sample of soap said to be made of 100 parts fat to 40 of rosin, and therefore containing 28.67 per cent. rosin, assayed by the volumetric method, 73.7 per cent. fatty acid, and by the gravimetric method, 25.7 per cent. rosin.

Unsaponifiable matter in the fat does not affect the process, but can be determined by the volumetric method in one operation, as

follows: Two gms. of the original fatty mixture are titrated with normal NaOH solution and saturate a cc. Two gms. are treated with HCl gas, etc., then titrated and saturate b cc. Then

$$b \times .346 = \text{weight of rosin.}$$

$$a - b \times .275 = \text{weight of f. a.}$$

The remainder is unsaponifiable matter.

A mixture of rosin, fatty acid and paraffine was prepared and analyzed in this manner, with the following results:

	Calculated.	Found.
Rosin	21.3	22.6
Fatty Acid	43.6	42.7
Paraffine	35.1	34.7

I have since analyzed a number of samples of soaps and always obtained the rosin distinctly brittle and therefore practically free from fat. This I found to be the case even when the percentage of rosin was so low as 4 or 5 per cent.

In my experiments the caustic soda solution was normal, but a more dilute solution might be used with advantage, as a smaller sample could be taken and the operation considerably hastened.

The figures given have been those actually obtained, without correction for error, such as unsaponifiable matter in the original rosin, which would affect the gravimetric determination. The volumetric method I should prefer in all cases except where an examination of the rosin was desired.

THE MANUFACTURE OF NITRIC ACID.

BY EDWARD HART.

In a communication to the *Zeitschrift für angewandte Chemie* (1890, p. 507), Güttmann describes an apparatus for the condensation of nitric acid. This consists of a series of straight clay tubes joined together top and bottom by U shaped connecting pieces. The tubes are made in one piece and are air cooled. The uncondensed gases pass into a tower where they are condensed by water and the condensed acid passes into receivers below. The tubes used for cooling are made by Rohrmann. The walls of the tubes have a thickness of only 8 mm., and they are 2-5 meters long. This gives a large cooling surface, and the walls are much thinner than when stoneware balloons are used

for condensing. The author has also improved the form of the retort used. He considers the cylinder form obsolete because of the large amount of space occupied and the danger of frothing over, especially at the end of the distillation. Besides this it involves lading out of the contents at the end of distillation, a very disagreeable and troublesome operation, and the joints of the retort are continually leaking. A comparison of the ordinary and the proposed arrangement is given as follows :

Plant for a daily output of 1700 kilos strong Nitric Acid.	Best Old System.	Güttmann System.
Number of Retorts	8	4
Number of Condensation Batteries	8	4
Requisite Building Surface	447 sq. m.	122 sq. m.
Quality of the Nitric Acid	All strengths from 42 to 93 per cent. HNO_3	93 to 94 per cent. HNO_3
Amount of Nitric Acid	3 to 7	1 to 2

One of the best features of the new arrangement is that only about half the time is required to finish the distillation. By the old method 24 to 28 hours is required to finish the distillation so that, including the time necessary for discharging, cooling and charging again, a charge can be finished only every other day. With Güttmann's apparatus a charge may be finished, discharged, cooled and recharged within 24 hours. The retorts in Güttmann's system seem to be a modification of the old fashioned pot retort and are discharged by means of a gate, but exact details are not given. According to Güttmann the saving in a plant built according to his system is equal to about \$20,000.

Güttmann's paper is criticised in the same journal by J. H. Andersch.* Andersch points out that the result of a distillation depends upon the skill and care with which it is carried out. If the retort is heated too hot at any one time, decomposition results and the amount of nitrous acid increases; this is independent of the size and shape of the retort and depends entirely upon the temperature. The shape of the retort makes no difference in the amount of frothing, provided it is not charged too heavily, and the cylinder form is an advantageous one, because it allows of the most perfect utilization of the heat. The space required is over-

*Ztschr. angew. Chem. 1890, 619.

rated by Güttmann; and while the tube system will no doubt promote rapid condensation, the number of joints is enormously increased, leading to trouble from leakage. The saving effected by Güttmann's system is also greatly overestimated, because a complete plant by the ordinary system for a production of 1700 kilos daily can be built for \$7500.

In a hectographic circular issued by Rohrmann to accompany a trade reprint of the original article of Güttmann's some additional particulars are given as follows: The amount of nitre charged in each pot is 600 kilos, and this can be distilled in 12 to 14 hours. Thirty kilos of coal are used for 100 kilos of strong acid, or 1 part coal produces rather more than 3 parts acid. The oxides of nitrogen formed amount to 1-2 per cent., according to the care taken. The yield of strong nitric acid (93 to 96 per cent.) is from the above charge, $437\frac{1}{2}$ kilos, not deducting oxides of nitrogen. It is stated that the National Explosives Co., of London, is now producing from 24 cwt. of moist saltpetre, 18 cwt. 4 lbs. of strong acid of 1.515 sp. gr.

In a subsequent notice* Güttmann gives some further details obtained from 2 months working of a plant in England constructed according to his system. The charge here used is 12 cwt. crude soda saltpetre and 13 cwt. oil of vitrol and the yield is 8.05 cwt. acid of 95.11 per cent. The N_2O_4 calculated as HNO_3 equals 2.58 per cent. and the loss of acid is 11.95 per cent. In this system however there is no tower, since only strong acid can be used.

I have recently designed and built a plant with a daily capacity of about this amount (more exactly 1600 kilos), and since its erection have watched carefully its performance. While the plant has not yet been run to its full capacity, sufficient data have been accumulated to give a fair idea of what can be done. Details can not be given for commercial reasons; but it may be stated that the entire cost of the plant, including the cost of the additional buildings for loading and unloading supplies, storage of nitre, nitre cake, acid, empty carboys, carboy boxes, salt hay for packing and coal storage was as nearly as can be determined \$4000. This includes the retorts, condensing apparatus and sufficient containers to hold one day's output, but does not include the cost of

*Ztsch. Angew. Chem. 1891, 238.

the land. The floor space of the retort house is 96 sq. m. Each retort holds a charge of 1100 lbs. of nitre, from which, when the operation is properly conducted, 880 lbs. of acid, sp. gr. 1.49, are produced in 13 hours. The yield and strength of acid of course vary slightly according to the character of the nitre (whether wet or dry), and the strength of the vitrol used; stronger acid (about 1.51), is generally produced. The condensation is effected entirely in glass and the product is of a very light yellow and as pure as it is possible to get nitric acid by one distillation. The system is such that nitric acid of any required strength can be obtained, from 1.54 sp. gr. which comes over at first to a product which runs less than 1.10 sp. gr. at the end of the operation. The nitre cake obtained is entirely free from nitric acid and is self-discharged from the retorts, which have a cylindrical form. About 7 lbs. of acid are obtained from each pound of coal used. Güttmann can obtain only a little more than 3 lbs. for the same fuel consumption. I regard this great difference as due mainly to the cylindrical form of my retort, the result confirming Andersch's view. I hope to be able to give some more definite figures after some changes now in prospect are made which will allow of a more careful analytical examination of materials and product.

**REPORT OF A SCIENTIFIC COMMISSION APPOINTED
BY HON. JOHN W. MASON, COMMISSIONER
OF INTERNAL REVENUE,**

**FOR THE PURPOSE OF ESTABLISHING STANDARDS AND METHODS
FOR THE POLARIMETRIC ESTIMATION OF SUGARS,**

**TO BE USED IN ASCERTAINING THE BOUNTY TO BE PAID UPON SUGARS OF
DOMESTIC PRODUCTION, AND FOR THE PURPOSE OF SECURING
UNIFORMITY IN SUCH STANDARDS AND METHODS.***

HON. JOHN W. MASON, *Commissioner Internal Revenue*—

Sir: The object and constitution of this Commission, the members of which were appointed at your request by the heads of their respective offices, are sufficiently indicated by the following letter of instructions :

TREASURY DEPARTMENT,
OFFICE OF INTERNAL REVENUE.

WASHINGTON, D. C., March 12, 1891.

DR. C. A. CRAMPTON, *Chemist Internal Revenue Bureau*—

Sir: You are hereby instructed to act as one member of a Commission consisting of the Chief Chemist of the Department of Agriculture, an expert

*Mss. sent by Dr. C. A. Crampton.

from the Coast and Geodetic Survey, and yourself, to confer together concerning the standardization of polariscopes, and the methods for the optical estimation of sugars, and for the purpose of securing uniform standards and methods. You will act as Chairman of the Commission, which will report directly to me upon the completion of the investigation, in order that its recommendations may be utilized in the preparation of the regulations for the polarization of sugars upon which a bounty is paid.

Respectfully,

(Signed)

JOHN W. MASON, *Commissioner*.

Section I, paragraph 231 of the Act entitled "an Act to reduce revenue and equalize duties on imports, and for other purposes," approved October 1, 1890, provides:

That on and after July 1, 1891, and until July 1, 1905, there shall be paid, from any moneys in the Treasury not otherwise appropriated, under the provisions of section 3,689 of the Revised Statutes, to the producer of sugar testing not less than ninety degrees by the polariscope, from beets, sorghum, or sugar-cane grown within the United States, or from maple sap produced within the United States, a bounty of two cents per pound; and upon such sugar testing less than ninety degrees by the polariscope, and not less than eighty degrees, a bounty of one and three-fourths cents per pound, under such rules and regulations as the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury, shall prescribe.

It is the opinion of this Commission that the expression "testing * * * *degrees* by the polariscope" used with reference to sugar in this Act, is to be considered as meaning the per cent. of pure sucrose the sugar contains, as ascertained by polarimetric estimation.

It is evident that a high degree of accuracy is necessary in the examination of sugars by the Bureau of Internal Revenue, under the provisions of this Act, inasmuch as the difference of one-tenth of one per cent. in the amount of sucrose contained in a sugar, may, if it is on the border line of 80 degrees, decide whether the producer is entitled to a bounty of $1\frac{3}{4}$ cents per pound, (an amount nearly equivalent to the market value of such sugar) or to no bounty whatever. It is desirable, therefore, that the highest possible degree of accuracy should be secured in the work, for while many sugars will doubtless vary far enough from the two standard percentages fixed upon in the Act, viz., 80 and 90 degrees, to admit of a wide margin of error without material consequence, yet a considerable proportion will approximate them so

closely, that a difference of a few tenths of a degree in the polarization will change the classification of the sugar.

A very high degree of accuracy may be obtained in the optical estimation of sugars, if the proper conditions are observed. Such conditions are, first, accurately graduated and adjusted instruments, weights, flasks, tubes, etc.; second, skilled and practised observers; third, a proper arrangement of the laboratories in which the work is performed; and fourth, a close adherence to the most approved methods of manipulation.

On the other hand, if due observance is *not* paid to these conditions, the sources of error are numerous, and inaccurate results inevitable.

We will endeavor to point out in this report the best means of meeting the proper conditions for obtaining the highest degree of accuracy consistent with fairly rapid work. It would be manifestly impossible to observe too great a refinement of accuracy in this work, such as would be employed in exact scientific research. This would be unnecessary for the end in view, and impossible on account of the amount of time that would be required.

I. INSTRUMENTS AND APPARATUS.

It is of the greatest importance that the polariscopes and all the apparatus used in the work shall be carefully and accurately adjusted and graduated, *and upon a single and uniform system of standardization*. Recent investigations of the polarimetric work done in the customs branch of the Treasury Department have shown, that a very considerable part of the want of agreement in the results obtained at the different ports was due to a lack of uniformity in the standardization of the instruments and apparatus.

(a) *The Polariscopes*.—There are many different forms of this instrument used. Some are adapted for use with ordinary white light, and some with monochromatic light, such as the sodium ray. They are graduated and adjusted upon various standards, all more or less arbitrary. Some, for example, have their scales based upon the displacement of the polarized ray produced by a quartz plate of a certain thickness; others upon the displacement produced by an arbitrary quantity of pure sucrose, dissolved and made up to a certain volume and polarized in a certain definite length of column. It would be very desirable to have an absolute

standard set for polariscopic measurements, to which all instruments could be referred, and in the terms of which all such work could be stated. This Commission has information that an investigation is now in progress under the direction of the German Imperial Government, having for its end and purpose the determination of such data as will serve for the establishment of an absolute standard. When this is accomplished, it can easily be made a matter of international agreement, and all future forms of instruments be based upon it. This Commission would suggest that the attention of the proper authorities should be called to the desirability of official action by this Government looking to its coöperation with other countries for the adoption of international standards for polarimetric work. Until this is done, however, it will be necessary for the Internal Revenue Bureau to adopt, provisionally, one of the best existing forms of polariscope, and by carefully defining the scale of this instrument, establish a basis for its polarimetric work which will be a close approximation to an absolute standard, and upon which it can rely in case of any dispute arising as to the results obtained by the officers of the Bureau.

For the instrument to be provisionally adopted by the Internal Revenue Bureau, this Commission would recommend the "half shadow" instrument made by Franz Schmidt & Haensch, Berlin. This instrument is adapted for use with white light illumination, from coal oil or gas lamps. It is convenient and easy to read, requiring no delicate discrimination of colors by the observer, and can be used even by a person who is color blind. This form of instrument is adjusted to the Ventzke scale, which, for the purposes of this report, is defined to be such that *one degree of the scale is the one-hundreth part of the rotation produced in the plane of polarization of white light in a column 200 mm. long, by a standard solution of chemically pure sucrose at 17.5° C. The standard solution of sucrose in distilled water being such as to contain, at 17.5° C. in 100 cc., 26.048 gms. of sucrose.*

In this definition the weights and volumes are to be considered as *absolute*, all weighings being referred to a vacuum. The definition should properly be supplemented with a statement of the equivalent *circular* rotation in degrees, minutes and seconds, that would be produced by the standard solution of sugar used to read

100 degrees on the scale. This constant is now a matter of investigation, and it is thought best not to give any of the hitherto accepted values. When this is established it is recommended that it be incorporated in a revision of the regulations of the Internal Revenue relative to sugar, in order to make still more definite and exact the official definition of the Ventzke scale.

The instruments should be adjusted by means of control quartz plates, three different plates being used for complete adjustment, one reading approximately 100 degrees on the scale, one 90, and one 80 degrees.

These control quartz plates should have their exact values ascertained in terms of the Ventzke scale by the Office of Weights and Measures by comparison with the standard quartz plates in possession of that office, in strict accordance with the foregoing definition, and should also be accompanied by tables giving their values for temperatures from 10 to 35 degrees.

(b) *Weights*.—The weights used should be of solid brass, and should be standardized by the Office of Weights and Measures.

(c) *Flasks*.—The flasks used should be of such a capacity as to contain, at 17.5° C. 100.06 cubic centimeters, when filled in such a manner that the lowest point of the meniscus of the surface of the liquid just touches the graduation mark. The flasks will be standardized to contain this volume in order that the results shall conform to the scale recommended for adoption, without numerical reduction of the weighings to vacuo. They should be calibrated by the Office of Weights and Measures.

(d) *Tubes*.—The tubes used should be of brass or glass, 200 and 100 millimeters in length, and should be measured by the Office of Weights and Measures.

(e) *Balances*.—The balances used should be sensitive to at least one milligram.

II. SKILLED OBSERVERS.

The Commission recommends that the work of polarizing sugars be placed in the hands of chemists, or at least of persons who are familiar with the use of the polariscope and have some knowledge of the theory of its construction, and of chemical manipulations. To this end we would suggest that applicants for positions where

such work is to be done should be obliged to undergo a competitive examination in order to test their fitness for the work that is to be required of them.

III. ARRANGEMENT OF LABORATORIES.

The arrangement of the rooms in which polarizations are performed has an important bearing upon the accuracy of the results obtained.

Polariscopic observations are made more readily and accurately if the eye of the observer is screened from diffused light, therefore a partial darkening of the room, which may be accomplished by means of curtains or hangings, is an advantage. On the other hand, the temperature at which the observation is made has a very considerable influence upon the results obtained, so that the arrangements for darkening the room must not be such as will interfere with its proper ventilation. Otherwise the heat from the lamps used, if confined within a small room, will cause considerable variations in the temperature of the room from time to time.

The proper conditions will best be met, in our opinion, by placing the lamps either in a separate room from that in which the instruments are, and perforating the wall or partition between the two rooms for the light to reach the end of the instrument, or in a ventilated hood with the walls perforated in a like manner. By lining the wall or partition on both sides with asbestos paper, and inserting a plate of plane glass in the aperture through which the light passes, the increase of temperature from the radiation of the lamp will be still further avoided.

With the lamps separated from the instruments in this manner, the space in which the latter are contained is readily darkened without much danger of its temperature being unduly raised. Some light, of course, is necessary for reading the scales, and if artificial light is employed for this purpose, the sources chosen should be such that as little heat as possible will be generated by them. Small incandescent electric lights are best for such purpose. Refinements of this kind cannot always be used, of course, but the prime requisite with reference to the avoidance of temperature errors is, that all operations, filling the flasks and tubes, reading the solutions, controlling the instrument with standard

quartz plates, etc., should be done at one and the same temperature, and that this temperature be a constant one, that is, not varying greatly at different hours of the day. For example, the room should not be allowed to become cold at night so that it is at a low temperature in the morning when work is begun, and then rapidly heated up during the day. The polariscope should not be exposed to the direct rays of the sun during part of the day, and should not be near artificial sources of heat, such as steam boilers, furnaces, flues, etc.

The tables upon which the instruments stand should be level.

IV. METHODS OF MANIPULATION.

The methods of manipulation used in the polarization of sugar are of prime importance. They consist in weighing out the sugar, dissolving it, clarifying the solution, making it up to standard volume, filtering, filling the observation tube, regulating the illumination, and making the polariscopic reading.

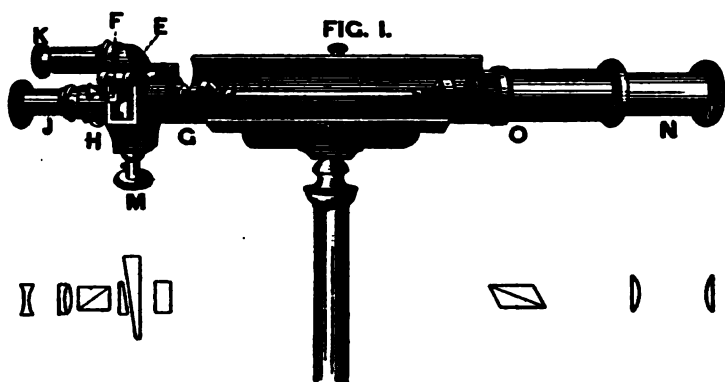
The proper conduct of these processes, in connection with the use of accurately graduated apparatus, is the only surety against the numerous sources of error which may be encountered. Different sugars require different treatment in clarification, and much must necessarily be left to the judgment and experience of the operator. The following directions are based upon various official procedures, such as the one used in the United States Custom Houses, the method prescribed by the German Government, etc. They embody also the result of recent research in regard to sources of error in the polarimetric estimation of sugar.

DIRECTIONS FOR THE POLARIZATION OF SUGARS.

DESCRIPTION OF INSTRUMENT AND MANNER OF USING.

The instrument employed is known as the half shadow apparatus of Schmidt & Haensch. It is shown in the following cut.

The tube *N* contains the illuminating system of lenses and is placed next to the lamp; the polarizing prism is at *O* and the analysing prism at *H*. The quartz wedge compensating system is contained in the portions of the tube marked *F*, *E*, *G*, and is controlled by the milled head *M*. The tube *J* carries a small telescope, through which the field of the instrument is viewed, and just above is the reading tube *K*, which is provided with a mirror and magnifying lens for reading the scale.



The tube containing the sugar solution is shown in position in the trough between the two ends of the instrument. In using the instrument the lamp is placed at a distance of at least 200 mm. from the end; and the observer seats himself at the opposite end in such a manner as to bring his eye in line with the tube *J*. The telescope is moved in or out until the proper focus is secured so as to give a clearly defined image, when the field of the instrument will appear as a round, luminous disk, divided into two halves by a vertical line passing through its centre and darker on one-half the disk than on the other. If the observer, still looking through the telescope, will now grasp the milled head *M* and rotate it, first one way and then the other, he will find that the appearance of the field changes, and at a certain point the dark half becomes light, and the light half dark. By rotating the milled head delicately backwards and forwards over this point he will be able to find the exact position of the quartz wedge operated by it, in which the field is neutral, or of the same intensity of light on both halves. The three different appearances presented by the field are best shown in the following diagram :



With the milled head set at the point which gives the appearance of the middle disk as shown above, the eye of the observer is raised to the reading tube *K* and the position of the scale is noted. It will be seen that the scale proper is attached to the quartz wedge, which is moved by the milled head; and attached to the

other quartz wedge, is a small scale called a *vernier*, which is fixed, and which serves for the exact determination of the position of the movable scale with reference to it. On each side of the zero line of the vernier a space corresponding to *nine* divisions of the movable scale is divided into *ten* equal parts. By this device the fractional part of a degree indicated by the position of the zero line is ascertained in tenths; it is only necessary to count from zero, until a line is found which makes a continuous line with one on the movable scale.

With the neutral field as indicated above, the zero of the movable scale should correspond closely with the zero of the vernier unless the zero point is out of adjustment.

If the observer desires to secure an *exact* adjustment of the zero of the scale, or in any case if the latter deviates more than one-half of a degree, the zero lines are made to coincide by moving the milled head and securing a neutral field at this point by means of the small key which comes with the instrument, and which fits a small nipple on the *left* hand side of *F*, the fixed quartz wedge of the compensating system. This nipple must not be confounded with the similar nipple on the *right* hand side of the analyzing prism *H*, which it fits as well, but which *must never be touched*, as the adjustment of the instrument would be seriously disturbed by moving it. With the key on the proper nipple it is turned one way or the other until the field is neutral. Unless the deviation of the zero be greater than .5 degree, it will not be necessary to use the key but only to note the amount of the deviation, and for this purpose the observer must not be content with a single setting, but must perform the operation five or six times and take the mean of these different readings. If one or more of the readings show a deviation of more than .3 degrees from the general average, they should be rejected as incorrect. Between each observation the eye should be allowed 10 or 20 seconds of rest.

The "setting" of the zero having been performed as above, the determination of the accurate adjustment of the instrument by means of the "control" quartz plates is proceeded with.

Three such plates will be furnished with each polariscope which have "sugar values," respectively, approximating 80, 90 and 100 degrees. These values vary with the temperature, and tables are

furnished with them which give their exact value at different temperatures from 10 to 35° C.

One of these plates is placed in the instrument, and the field observed; it will be seen that the uniform appearance of the field is changed. The milled head is turned to the right until the exact point of neutrality is re-established, just as described above in setting the zero. The scale is read, the observation repeated, the reading taken again, and so on until five or six readings have been made. The average is taken, readings being rejected which show a divergence of more than .3, and the result corrected for the deviation of the zero point, if any was found, the deviation being added if it was to the left, and subtracted if to the right. If the adjustment of the instrument be correct, the result should be the value of the control plate used, as ascertained from the table, for the temperature of 20 degrees. Each of the three plates is read in the instrument in this way. A variation of .3 from the established values may be allowed for errors of observation, temperature, etc., but in the hands of a careful observer, *a deviation greater than this with any one of the three plates after a careful setting of the zero, shows that the instrument is not accurately adjusted.*

The complete verification of the accurate adjustment of the polariscope by means of three control plates, as given above, should be employed whenever it is set up for the first time by the officers using it, whenever it has sustained any serious shock or injury, and whenever it has been transported from one place to another. It should also be done at least once a week while the instrument is in active use.

After the complete verification has been performed as described, further checking of the instrument is done by means of one control plate alone, the one approximating 90 degrees, and the setting of the zero point is dispensed with, the indication of the scale for sugar solutions being corrected by the amount of deviation shown in the reading of the 90 degree control plate from its established value as ascertained from the table, at the temperature of the room.

For example: A sugar solution polarizes 80.5; the control plate just before had given a polarization of 91.4, the temperature of the room during both observations being 25° C. According to the table the value of the control plate at 25° C. is 91.7; the reading

is therefore .3 too low and .3 is added to the reading of the sugar solution, making the corrected result 80.8. The temperature of the room should be ascertained from a standardized thermometer placed close to the instrument and in such a position as to be subject to the same conditions.

PREPARATION OF THE SUGAR SOLUTION FOR POLARIZATION.

If the sample is not entirely uniform it must be thoroughly mixed before weighing out, after all the lumps are broken up, best with a mortar and pestle. Then 26.048 gms. are weighed out on the balance in the tared German silver dish furnished for this purpose. Care must be taken that the operations of mixing and weighing out are not unduly prolonged, otherwise the sample may easily suffer a considerable loss of moisture, especially in a warm room. The portion of sugar weighed out is washed by means of a jet from a wash bottle into a 100 cc. flask, the dish being well rinsed three or four times and the rinsings added to the contents of the flask. The water used must be either distilled water, or clear water which has been found to have no optical activity.

After the dish has been thoroughly rinsed, enough water is added to bring the contents of the flask to about 80 cc., and it is gently rotated until all the sugar has dissolved. The flask should be held by the neck with the thumb and finger, and the bulb not handled during this operation. Care must be taken that no particle of the sugar or solution is lost. To determine if all the sugar is dissolved, the flask is held above the level of the eye, in which position any undissolved crystals can be easily seen at the bottom.

The character of the solution is now observed. If it be colorless or of a very light straw color, and not opalescent, so that it will give a clear, transparent liquid on filtration through paper, the volume is made up directly with water to the 100 cc. mark on the flask. Most sugar solutions, however, will require the addition of a clarifying or decolorizing agent in order to render them sufficiently clear and colorless to polarize. In such case, before making up to the mark, a saturated solution of subacetate of lead is added.

The quantity of this agent required will vary according to the quality of the sugar; for sugar which has been grained in the strike pan and well washed in the centrifugals, from 3 to 15 drops will be required; for sugar grained in the strike pan but not well washed in the centrifugals, that is, sugar intended for refining purposes, from 15 to 30 drops will be required; for sugar not grained in the strike pan, that is, "wagon" or "string" sugar, "open kettle sugar," etc., from 1 to 3 cc. will be required. After adding the solution of subacetate of lead the flask must be gently shaken, so as to mix it with the sugar solution. If the proper amount has been added, the precipitate will usually subside rapidly, but if not the operator may judge of the completeness of the precipitation by holding the flask above the level of the eye and allowing an additional drop of subacetate of lead to flow down the side of the flask into the solution; if this drop leaves a clear track along the glass through the solution it indicates that the precipitation is complete; if, on the other hand, all trace of the drop is lost on entering the solution, it indicates that an additional small quantity of the subacetate of lead is required. The operator must learn by experience the point where the addition should cease; *a decided excess of subacetate of lead solution should never be used.*

The use of subacetate of lead should, in all cases, be followed by the addition of "alumina cream," (aluminic hydrate suspended in water)* in about double the volume of the subacetate solution used, for the purpose of completing the clarification, precipitating excess of lead, and facilitating filtration. In many cases of high grade sugars, especially beet sugars, the use of alumina cream alone will be sufficient for clarification without the previous addition of subacetate of lead.

*Prepared as follows: Shake up powdered commercial alum with water at ordinary temperatures until a saturated solution is obtained. Set aside a little of the solution, and to the residue add ammonia, little by little, stirring between additions, until the mixture is alkaline to litmus paper. Then drop in additions of the portion set aside until the mixture is just acid to litmus paper. By this procedure a cream of aluminum hydroxide is obtained suspended in a solution of ammonium sulphate, the presence of which is not at all detrimental for sugar work when added after subacetate of lead, the ammonium sulphate precipitating whatever excess of lead may be present.

The solution is now made up to the mark by the addition of distilled water in the following manner. The flask, grasped by the neck between the thumb and finger, is held before the operator in an upright position, so that the mark is at the level of the eye, and distilled water is added, drop by drop, from a siphon bottle or wash bottle, until the lowest point of the curve or meniscus formed by the surface of the liquid just touches the mark. If bubbles hinder the operation, they may be broken up by adding a single drop of ether, or a spray from an ether atomizer, before making up to the mark. The mouth of the flask is now tightly closed with the thumb, and the contents of the flask are thoroughly mixed by turning and shaking. The entire solution is now poured upon the filter, using for this purpose a funnel large enough to contain all the 100 cc. at once, and a watch glass is placed over the funnel during filtration, to prevent a concentration of the solution by evaporation. The funnel and the vessel used to receive the filtrate must be perfectly dry. The first portion of the filtrate, about 20 to 30 cc. should be rejected entirely, as its concentration may be affected by a previous hygroscopic moisture content of the filter paper. It may also be necessary to return subsequent portions to the filter until the liquid passes through perfectly clear.

If a satisfactory clarification has not been obtained, the entire operation must be repeated, since *only with solutions that are entirely clear and bright can accurate polarimetric observations be made.*

When a sufficient quantity of the clear liquid has passed through the filter, the 200 mm. observation tube is filled with it. (The 100 mm. tube should never be used except in the rare cases, when, notwithstanding all the means used to effect the proper decolorization of the solution, it is still too dark to polarize in the 200 mm. tube. In such cases the shorter tube may be used, and its reading multiplied by two. The zero deviation must then be determined and applied to the product. This will give the reading which would have been obtained if a 200 mm. tube should have been used, and it only remains to apply the correction determined by the use of the control plate as previously described.

Example (taken at a Temperature of 33° C.)

Solution reads in 100 mm. tube	47.
Multiplied by 2	2
Product	= 94.
Zero reads + 0.3	— 0.3
Solution would read in 200 mm. tube	93.7
Reading of control plate	90.4
Sugar value of control plate	90.5
Instrument too low by	0.1
Add 0.1 to	93.7
Correct polarization of solution	93.8)

Before filling the tube it must either be thoroughly dried by pushing a plug of filter paper through it, or it must be rinsed several times with the solution itself. The cover glasses must also be clean and dry, and without serious defects or scratches. Unnecessary warming of the tube by the hand during filling should be avoided; it is closed at one end with the screw cap and cover glass, and grasped at the other end with the thumb and finger. The solution is poured into it until its curved surface projects slightly above the opening, the air bubbles allowed time to rise, and the cover glass pushed horizontally over the end of the tube in such a manner that the excess of liquid is carried over the side, leaving the cover glass exactly closing the tube with no air bubbles beneath it, and with no portion of the liquid upon its upper surface. If this result is not attained, the operation must be repeated, the cover glass being rubbed clean and dry, and the solution again brought up over the end by adding a few more drops. The cover glass being in position, the tube is closed by screwing on the cap. The greatest care must be observed in screwing down the caps that they do not press too tightly upon the cover glasses; by such pressure the glasses themselves may become optically active, and cause erroneous readings when placed in the instrument. It should therefore be ascertained that the rubber washers are in position over the cover glasses, and the caps should be screwed on lightly. It must also be remembered that a cover glass, once compressed, may part with its acquired optical activity very slowly,

and some time must be allowed to elapse before it is used again.

The polariscopic reading may now be taken, an observation on the 90 degree control plate having been made immediately before as previously described. *Then without altering the position of the instrument relative to the light, or changing the character of the latter in any way*, the tube filled with the sugar solution is substituted for the control plate. The telescope is adjusted, if necessary, so as to give a sharply defined field, which must appear round and clear. (This condition *must be fulfilled* before the observation is performed, as it is essential to accuracy.) The milled head is turned until the neutral point is found, and the reading is taken exactly as previously described, the operation repeated 5 or 6 times, the average taken with the rejection of aberrant readings, the average figure corrected for the deviation shown by the control observation from the sugar value of the control plate at the temperature of observation as given in the table, and the result taken as the polarization of the sugar. When a series of successive polarizations is made under the same conditions as regards temperature, position of the instrument with relation to the light, intensity of the light, etc., the control observation need not be made before each polarization, one such observation being sufficient for the entire series. The control must be repeated at least once an hour, however, and oftener whenever the operator has reason to think that any of the factors indicated above have been altered, for any such alteration of conditions may change the zero point of the instrument.

In the polarization of the quartz plates, as also in the polarization of very white sugars, difficulty may be experienced in obtaining a complete correspondence of both halves of the field. With a little practice this may be overcome and the neutral point found, but when it cannot, the ordinary telescope of the instrument may be replaced by another, which is furnished with the polariscope, and which carries a yellow plate. This removes the difficulty, and renders it possible, even for one not well accustomed to the instrument, to set it at the exact point of neutrality.

SUMMARIZED SOURCES OF ERROR.

The following principal sources of error must be especially guarded against:

1. Drying out of sample during weighing.
2. Excess of subacetate of lead solution in clarification.
3. Incomplete mixing of solution after making up to mark.
4. Imperfect clarification or filtration.
5. Concentration of solution by evaporation during filtration.
6. Undue compression of the cover glasses.
7. Alteration of the temperature of room, position of instrument, or intensity of light while the observation or control observation are being performed.
8. Performance of polarization with a cloudy, dim, or not completely round and sharply defined field.

In closing this report the members of this Commission hereby signify their intention to promote uniformity and accuracy by adopting and using the standards and the general plan of procedure recommended in this report in the polarimetric determinations over which, in their respective branches of Government work, they have control.

Respectfully submitted,

(Signed)

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Washington, D. C., June 10, 1891.

STUDY OF A METHOD FOR THE QUANTITATIVE DETERMINATION OF SUCROSE, INVERT- SUGAR AND DEXTROSE, OR LEVULOSE.

BY F. G. WEICHMANN, PH.D.

PART II.

For reasons indicated in Part I, of this article,* a careful investigation was made concerning the various conditions which affect the destruction of the levulose on treatment with hydrochloric acid. It soon became patent that in order to gain a clear understanding of the problem, like attention would have to be given to the behavior of invert-sugar and of dextrose, under similar conditions; in consequence, this investigation was extended considerably beyond the limits originally intended.

The results obtained are recorded in seven "Series of Experiments," which are given below:

For valuable and conscientious work performed in the securing of these data, the writer acknowledges his indebtedness to his assistants, Messrs. Brainerd and Ziebolz.

All determinations refer to 0.25 gram, dry substance.

Invert-sugar, dextrose, and levulose were each separately studied with reference to variations in:

- a. The time of boiling.
- b. The amount of acid.
- c. The time of boiling against the amount of acid.

These tests are given in Series 1, 2 and 3.

Series 4 and 5, treat of the behavior, under like variations of condition, of mixtures of invert-sugar and dextrose, and of invert-sugar and levulose, 94.0 per cent. of the former to 6.0 per cent., respectively, of dextrose and of levulose.

Series 6 exhibits the behavior of invert-sugar and dextrose, mixed in different proportions, when exposed under the same conditions as to time of boiling and amount of acid present.

Series 7 shows a parallel set of tests, carried out on corresponding mixtures of invert-sugar and levulose.

*The School of Mines Quarterly, Vol. 11, No. 3, 1890. This Jour., Vol. 4, p. 253.

SERIES I.—INVERT-SUGAR.

0.25 gm. of dry substance used in each experiment.

Conditions varied : Time of Boiling.		Condition varied : Amount of Acid.		Conditions varied : Time of Boiling and amount of Acid.	
60 cc. HCl (6 x normal strength) were used in each experiment.		Time of Boiling : Four hours in each experiment.			
Time of boiling, in hours.	If all levulose, and only levulose, were destroyed, there would be reduced of Cu = 0.2355. There were reduced of Cu :	Am't of HCl (6 x normal strength) used.	If all levulose, and only levulose, were destroyed, there would be reduced of Cu = 0.2355. There were reduced of Cu :	Time of boiling in hours : am't of HCl (6 x normal strength) used.	If all levulose, and only levulose were destroyed, there would be reduced of Cu = 0.2381. There were reduced of Cu :
1	0.2632 } 0.2675 } 0.2668 0.2698 }	30 cc.	0.2564 } 0.2609 } 0.2587	3 hours. 120 cc.	0.2223 } 0.2254 } 0.2239
2	0.2546 } 0.2591 } 0.2568	60 cc.	0.2350 } 0.2362 } 0.2356	6 hours. 60 cc.	0.2290 } 0.2300 } 0.2295
3	0.2490 } 0.2492 } 0.2491	90 cc.	0.2147 } 0.2184 } 0.2166		
4	0.2350 } 0.2362 } 0.2356				
6	0.2232 } 0.2267 } 0.2249				

Inspection of Series No. 1, invert-sugar, teaches :

1. That, working with the prescribed amount of hydrochloric acid of six times the normal strength, a boiling time of four hours is necessary to effect complete destruction of the levulose present.

2. That boiling continued beyond this time results in partial destruction of the dextrose.

3. That the time of boiling being the same, the action which the acid exerts upon the invert-sugar is directly proportional to the amount of acid present ; that is to say, insufficient acid will leave some levulose undestroyed ; excess of acid will destroy some dextrose in addition to the levulose.

4. That the time of boiling and the amount of acid used are directly interchangeable ; that is to say, that practically the same results are obtained by boiling for three hours with 120 cc. of acid as by boiling six hours with 60 cc. of acid.

SERIES II.—DEXTROSE.

0.25 gm. dry substance used in each experiment.

Condition varied : Time of Boiling.		Condition varied : Amount of Acid.		Conditions varied : Time of Boiling and amount of Acid.	
60 cc. HCl (6 x normal strength) were used in each experiment.		Time of Boiling : Four hours in each experiment.			
Time of boiling in hours.	If the dextrose were not attacked by the acid, there would be reduced of Cu=0.4505. There were reduced of Cu :	Am't of HCl (6 x normal strength) used.	If the dextrose were not attacked by the acid, there would be reduced of Cu=0.4505. There were reduced of Cu :	Time of boiling in hours : am't of HCl (6 x normal strength) used.	If the dextrose were not attacked by the acid, there would be reduced of Cu=0.4570. There were reduced of Cu :
1	0.4323 } 0.4337 0.4350 }	30 cc.	0.4282 } 0.4285 0.4288 }	3 hours. 120 cc.	0.2914 } 0.2944 0.2973 }
2	0.4270 } 0.4283 0.4296 }	60 cc.	0.3977 } 0.3982 0.3986 }	6 hours. 60 cc.	0.2901 } 0.2915 0.2929 }
3	0.4153 } 0.4163 0.4173 }	90 cc.	0.3852 } 0.3857 0.3861 }		
4	0.3977 } 0.3984 0.3986 }				
6	0.2901 } 0.2915 0.2929 }				

Inspection of Series No. 2 dextrose, shows :

1. That dextrose in solution is attacked by hydrochloric acid of six times the normal strength.
2. That the amount of acid used being constant, the amount of dextrose destroyed depends upon the length of time that the boiling is continued.
3. That the amount of dextrose thus destroyed is not the same for corresponding periods of time, but rapidly increases as the time of boiling is prolonged. Thus, the difference in the amounts of copper reduced, is : between one and two hours' boiling, 0.0054 ; between two and three hours boiling, 0.0120 ; between three and four hours' boiling, 0.0179 ; between four and six hours' boiling, 0.1069.
4. That the time of boiling being the same, the action which

the acid exerts upon the dextrose is proportional to the amount of the acid present—the more acid, the more dextrose is destroyed.

5. That the time of boiling, and the amount of acid used are, practically, interchangeable factors.

SERIES III.—LEVULOSE.

0.25 gm. dry substance used in each experiment.

Condition varied: Time of Boiling.		Condition varied: Amount of Acid.		Conditions varied: Time of Boiling and amount of Acid.	
60 cc. HCl (6 x normal strength) were used in each experiment.		Time of Boiling: Four hours in each experiment.			
Time of boiling, in hours.	Untreated levulose reduces of Cu=0.4290. If all levulose were destroyed, no Cu would be reduced. There were reduced of Cu:	Am't of HCl (6 x normal strength) used.	Untreated levulose reduces of Cu=0.4290. If all levulose were destroyed, no Cu would be reduced. There were reduced of Cu:	Time of boiling, in hours; am't of HCl (6 x normal strength) used.	Untreated levulose reduces of Cu=0.4228. If all levulose were destroyed, no Cu would be reduced. There were reduced of Cu:
1	0.2716 } 0.2731 0.2746 }	30 cc.	0.2620 } 0.2630 0.2640 }	3 hours. 120 cc.	0.0518 } 0.0545 0.0572 }
3	0.2082 } 0.2122 0.2162 }	60 cc.	0.0878 } 0.0882 0.0886 }	6 hours. 60 cc.	0.0468 } 0.0473 0.0477 }
4	0.0878 } 0.0882 0.0886 }	90 cc.	0.0370 } 0.0373 0.0376 }		
6	0.0468 } 0.0473 0.0477 }				

Series No. 3, levulose, shows:

1. That, the amount of acid being constant, the amount of levulose destroyed depends upon the length of time that the boiling is carried on.

2. That, the time of boiling being constant, the amount of levulose destroyed is proportional to the amount of acid used.

3. That the time of boiling, and the amount of acid used are, practically, interchangeable factors.

Series No. 4 and No. 5 (see pp. 405 and 406) exhibit the determinations made, respectively, on mixtures of invert-sugar (94 per cent.) with dextrose (6 per cent.), and with levulose (6 per cent.)

Both series show:

1. That, the amount of acid remaining constant, the time of

boiling determines the extent to which the sugars are decomposed.

2. That, the time of boiling remaining constant, the extent to which the decomposition is effected is dependent upon the amount of acid present.

3. That the time of boiling, and the amount of acid used are, practically, interchangeable factors.

All of these tests, made on mixtures of invert-sugar and dextrose, and invert-sugar and levulose, respectively, are simply confirmatory of the results obtained by the experiments made with these substances individually.

SERIES IV.—INVERT-SUGAR AND DEXTROSE.

(94.0 per cent.) + (6.0 per cent.)

0.25 gm. dry substance used in each experiment.

Condition varied: Time of Boiling,		Condition varied: Amount of Acid.		Conditions varied: Time of Boiling and amount of Acid.	
60 cc. HCl (6 x normal strength) were used in each experiment.		Time of Boiling: Four hours in each experiment.			
Time of boiling, in hours.	If all levulose, and only levulose were destroyed, there would be reduced of Cu=0.2526. There were reduced of Cu:	Am't of HCl (6 x normal strength) used.	If all levulose, and only levulose were destroyed, there would be reduced of Cu=0.2526. There were reduced of Cu:	Time of boiling, in hours; am't of HCl (6 x normal strength) used.	If all levulose, and only levulose were destroyed, there would be reduced of Cu=0.2526. There were reduced of Cu:
1	0.2848 } 0.2856 0.2864 }	60 cc.	0.2397 } 0.2413 0.2428 }	3 hours. 120 cc.	0.2289 } 0.2295 0.2300 }
2	0.2570 } 0.2585 0.2600 }	120 cc.	0.2080 } 0.2103 0.2126 }	6 hours. 60 cc.	0.2298 } 0.2307 0.2316 }
3	0.2497 } 0.2515 0.2533 }				
4	0.2397 } 0.2413 0.2428 }				
6	0.2235 } 0.2253 0.2270 }				

In addition to establishing these facts, Series 4 and 5 show—as was to be anticipated—that the length of time during which the boiling must be continued in order to destroy all of the levulose,

depends upon the amount of levulose present. Thus, in the mixture consisting of invert-sugar 94 per cent., plus dextrose 6 per cent., three hours yield a result most closely approximating the theoretical value; and, in the case of the mixture of invert-sugar 94 per cent. and levulose 6 per cent., four hours were needed to obtain this approximation.

SERIES V.—INVERT-SUGAR AND LEVULOSE.

(94.0 per cent.) + (6.0 per cent.)

0.25 gm. dry substance used in each experiment.

Condition varied: Time of Boiling.		Condition varied: Amount of Acid.		Conditions varied: Time of Boiling and amount of Acid.	
60 cc. HCl (6 x normal strength) were used in each experiment.		Time of Boiling: Four hours in each experiment.			
Time of boiling, in hours.	If all levulose, and only levulose were destroyed, there would be reduced of Cu = 0.2256. There were reduced of Cu.	Am't of HCl (6 x normal strength) used.	If all levulose, and only levulose were destroyed, there would be reduced of Cu = 0.2238. There were reduced of Cu:	Time of boiling, in hours; am't of HCl (6 x normal strength) used.	If all levulose, and only levulose were destroyed, there would be reduced of Cu = 0.2238. There were reduced of Cu:
1	0.2865 } 0.2870 0.2875 }	60 cc.	0.2280 } 0.2266 0.2252 }	3 hours. 120 cc.	0.2182 } 0.2167 0.2152 }
2	0.2404 } 0.2410 0.2416 }	120 cc.	0.1952 } 0.1969 0.1986 }	6 hours. 60 cc.	0.2088 } 0.2098 0.2108 }
3	0.2347 } 0.2359 0.2370 }				
4	0.2280 } 0.2266 0.2252 }				
6	0.2088 } 0.2098 0.2108 }				

Series No. 6 and No. 7 (see pp. 407 and 408) show the effect of a constant amount of acid, with constant time of boiling, on different mixtures of invert-sugar and dextrose, and of invert-sugar and levulose.

The values obtained in series No. 6, with one exception, (ratio 95:5), all show that *less* copper was reduced than should have been reduced.

The values in series No. 7 all show, without exception, that *more* copper was reduced than should have been reduced.

The significance of these data is evident.

In the case of invert-sugar (series No. 1), where the proportion of the dextrose to levulose is as 1 : 1, four hours' boiling with 60 cc. HCl (6 x normal strength) resulted in a destruction of the levulose almost theoretically perfect.

Series No. 6 demonstrates that, if the substance operated upon, under the same conditions named above, does not consist of dextrose and levulose in the proportion 1 : 1, but contains an *excess* of dextrose, *dextrose as well as levulose* is destroyed.

Series No. 7 demonstrates that, if the substance operated upon under the same conditions, does not consist of dextrose and levulose in the proportion 1 : 1, but contains an *excess* of levulose, *the levulose is not all destroyed*.

SERIES VI.—INVERT-SUGAR AND DEXTROSE.

0.25 gm. dry substance used in each experiment.

In each instance:

Time of boiling, 4 hours. Amount of HCl (6 x normal strength)=60 cc.

* Ratio of Invert-Sugar to Dextrose.	If all levulose, and <i>only</i> levulose were destroyed, there would be reduced of Cu:	There were reduced of Cu:
50 : 50	0.3460	0.3215 } 0.3217 0.3218 }
60 : 40	0.3238	0.3106 } 0.3109 0.3112 }
90 : 10	0.2572	0.2560 } 0.2567 0.2573 }
94 : 6	0.2526	0.2397 } 0.2413 0.2428 }
95 : 5	0.2462	0.2484 } 0.2491 0.2498 }
98 : 2	0.2392	0.2365 } 0.2383 0.2380 } 0.2405 }

It is therefore proved, that this method of analysis cannot serve

for the determination of the relative amounts of invert-sugar, dextrose, or levulose, when these occur together. The solution of this problem, if it is to be attempted on these lines, calls for the discovery of some reagent which will, under *all circumstances*, destroy absolutely the one of these sugars, dextrose or levulose, and not affect the other.

SERIES VII.—INVERT-SUGAR AND LEVULOSE.

0.25 gm. dry substance used in each experiment.

In each instance :

Time of boiling, 4 hours. Amount of HCl (6 x normal strength)=60 cc.

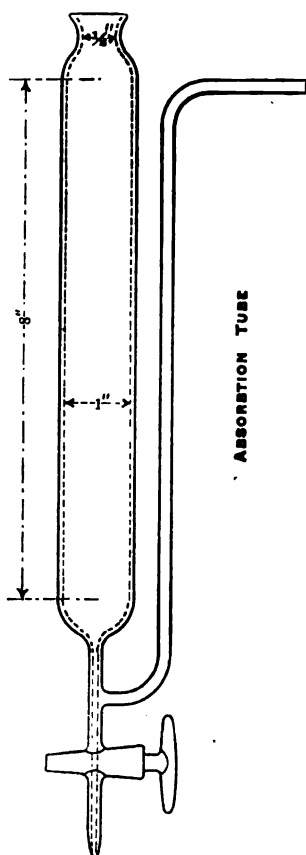
Ratio of Invert-Sugar to Levulose.	If all levulose, and <i>only</i> levulose were destroyed, there would be reduced of Cu:	There were reduced of Cu:
50:50	0.1177	0.1693 } 0.1706 0.1718 }
60:40	0.1413	0.1765 } 0.1768 0.1770 }
90:10	0.2119	0.2236 } 0.2242 0.2247 }
94: 6	0.2238	0.2280 } 0.2266 0.2252 }
95: 5	0.2233	0.2254 } 0.2282 0.2263 } 0.2303 } 0.2307 }
98: 2	0.2308	0.2410 } 0.2423 0.2410 } 0.2430 } 0.2440 }

Such a reagent would prove of the greatest value for the study of important problems in connection with the sugar industry, and by its aid we might also hope for the disclosure of some of the most closely guarded secrets of nature's laboratory—the formation of saccharine juices in the vegetable kingdom.

ABSORPTION APPARATUS FOR SULPHUR DETERMINATION.*

By J. M. CAMP.

The apparatus is filled, preferably, with short pieces of thin glass rods, shaken up in a bottle to round off the corners. The apparatus is then filled two-thirds full with saturated solution of Br in HCl, about 200 cc. to liter, and is ready for use.



*From Baker & Adamson's Prices Current.

A NEW METHOD OF SEPARATING IRON FROM COBALT AND NICKEL.

As is well known one of the best methods for estimating cobalt or nickel consists in subjecting to electrolysis the saline solution of these metals, alkaline, neutral or even slightly acid.

It is also well known that in this electrolytic treatment manganese which may be mixed with the cobalt or nickel does not interfere, since it is deposited at the positive pole under the form of hydrate of the peroxide, without carrying down with it any cobalt. But it is not the same with iron which must be previously separated by some one of the ordinary methods of precipitation. But the methods for the separation of iron from cobalt and nickel are long and tedious and the separations must be repeated several times in order to be complete. The method for the separation of iron by the voltaic current is as follows :

The metals present, viz : cobalt or nickel, manganese or iron in their maximum state of oxidation are brought into solution in the form of sulphates. To the solution is added a small quantity of organic acid, for instance, citric acid. There is next added, in large excess, a concentrated solution of sulphate of ammonium, rendered very strongly ammoniacal. Under these conditions, in the presence of citric acid, the peroxide of iron is not precipitated. There is now placed in the ammoniacal solution of the sulphates the platinum electrodes of any good electrolyzing battery. For instance, two elements of Bunsen giving off about 300 cc. of gas per hour. The manganese is deposited at the positive pole and the nickel or cobalt is deposited with the iron at the negative pole. After the metals have been completely deposited the current is broken. The negative electrode is withdrawn and is rapidly washed with boiling distilled water, and it is then placed in a concentrated solution of pure sulphate of ammonium, saturated with caustic ammonia. It is again connected with the battery and this time with the positive pole. Into the ammoniacal solution there is placed a second platinum electrode, previously weighed, which is connected with the negative pole. The current is now allowed to pass of such a strength as to give 100 cc. gas per hour. Under these conditions, the plate on which the cobalt, nickel and iron are deposited, plays the role of a soluble electrode. Under the

influence of the current the metals are oxidized, while the oxides of cobalt and nickel are dissolved in the ammoniacal liquor and are deposited in a metallic state upon the negative electrode. The iron transformed into insoluble ferric hydrate remains, in part, upon the negative electrode and floats, in part, in the electrolytic liquid. The precipitated ferric hydrate formed under these conditions does not carry down with it any appreciable traces of cobalt or nickel, and these metals are deposited in totality at the negative pole.—*G. A. LeRoy, Comptes Rendus, Vol. 112, No. 14, p. 722.*

H. W. W.

ON THE ESTIMATION OF NITROGEN IN ARABLE SOILS BY THE METHOD OF KJELDAHL.

Numerous difficulties have attended attempts to apply the Kjeldahl method for the estimation of nitrogen to samples of soil. Muller has modified the method to some extent and made comparisons of the quantity of nitrogen by this modified method and by the soda-lime method.

The principal difficulty encountered has been in the regular heating of the mixture of fuming sulphuric acid and soil. The particles of soil are deposited at the bottom of the flask and the result is that the bottom layers become overheated, and being poor conductors of heat, fail to transmit a sufficient quantity of heat to penetrate to the upper layers of the liquid to complete the reaction. In order to avoid this difficulty, Muller heats his flask in a small stove formed with a straight vertical cylinder of sheet iron or copper, the upper end of which is covered with a sheet of iron, pierced with a hole, which allows the neck of the flask to pass through, while the lower end is closed with a piece of sheet-iron furnished on its upper surface with a layer of asbestos. This cylinder of metal is surrounded with a second one, concentric with the first, through which passes a current of heated gases furnished by an ordinary Bunsen burner. By heating the flask in this stove or furnace, an even distribution of the heat is secured to all parts of the mixture, but the little drops of sulphuric acid which are condensed on the cold parts of the neck, sometimes lead to the fracture of the glass as they run down the sides of the flask to the hot portions. To prevent the reflux of this condensed acid, which

only needs to be done toward the end of the reaction, when it is necessary to heat to a very high temperature, the neck of the flask is bent at the point immediately above its emergence at the upper surface of the furnace, and the end of the neck is carried into a flask which will receive the drops of sulphuric acid condensed during the operation. The flask should have about 75 cc. capacity, and the curved portion of the neck is prevented from becoming cold during the process of heating by being covered with sheet-iron or some other material. The furnace has the following dimensions: height, 12 centimeters; diameter of interior of cylinder, 5.5 centimeters; diameter of exterior of cylinder, 7.5 centimeters.

The furnace is supported on a triangle of large iron wire and is heated by an ordinary Bunsen burner, or by a concentric Bunsen burner, according to the temperature which it is necessary to obtain. The proportions which should be observed between the amount of earth employed and the sulphuric acid are about as follows: of the dry earth, 15 gms.; of the fuming sulphuric acid, 30 cc. There should also be added to the mixture about .3 of a gm. of pure stearic acid, or better, benzoic acid. When the soil to be analyzed does not contain carbonate, the sulphuric acid should be added in two portions. At first add about 20 cc. of the acid and after shaking it the other 10 cc., running it in from a burette or pipette in such a manner as to wash thoroughly the neck and sides of the flask. If the earth contains carbonate, however, it is necessary to add the fuming acid in small portions of about 5 cc. at a time, waiting each time until the disengagement of gas, caused by the previous addition, has ceased. A soil which contains from 30 to 40 per cent. of carbonate of lime should be carefully treated in a porcelain capsule, with a slight excess of sulphuric acid, pure and dilute. The mixture is afterward to be evaporated to dryness upon a sand bath and the residue heated in a drying oven at 110 degrees. The mass is then pulverized, introduced into the flask, treated with .3 of a gm. benzoic acid and 30 cc. fuming sulphuric acid, treated as indicated above. In all cases it is necessary to continue the heating until the contents of the flask are colorless.

With soils containing considerable quantities of iron, however,

a slight red color will probably be observed which will not interfere with the accuracy of the tests.

The heating should at first be gentle, and the temperature afterward elevated little by little, and finally the heat should be sufficiently great to distill about 1.5 cc. sulphuric acid. The operation lasts from 12 to 18 hours. As the reaction is terminated, the cooled mass is taken up with water absolutely free from ammonia. It is filtered into a flask and washed upon the filter until the volume of the filtered liquid is about 350 cc. Afterward an excess of soda lye at 50° B. is added, then a few pieces of broken quartz to facilitate boiling. The flask is then connected with a condenser, the liquid distilled and received in a conical flask closed by a cork having two holes, of which one permits the entrance of the end of the condenser and the other a glass tube which is connected with a small flask containing water; the neck of the receiving flask being inclined toward the condenser to avoid the *entrainment* of any of the alkaline liquid which may be distilled. The receiving flask rests upon two or three pieces of sheet-iron and is heated with an ordinary burner, and ebullition is perfectly regular. From 170 to 180 cc. of the liquid are distilled in from three and a half to four hours. The distilled liquid, treated with a few drops of litmus, is titrated by a solution of sulphuric or hydrochloric acid of which 1 cc. corresponds to .001 cc. of nitrogen.

The determination of nitrogen in the soil by soda-lime is carried on as follows: 15 gms. of fine earth, dried and mixed with a little sugar, are mixed with 30 gms. soda-lime in powder; the bottom of the combustion tube contains a little moist soda-lime, which is heated at the end of the operation, at the same time that a current of pure hydrogen is made to pass through it, and the temperature of the tube is raised little by little to a distinct redness. The contents of the receiving bulbs are distilled, after the addition of water and soda, in the same apparatus which served in the estimation of nitrogen by the method of Kjeldahl, and the determinations and titrations are made also under the same conditions.

Blank determinations were also made under the same conditions in order to determine the amount of correction to be made by the two methods. Soda-lime heated with pure sugar gave .0002 of nitrogen for a total weight of 55 gms. of the soda-lime contained

in the tube. The fuming sulphuric acid gave .0011 of ammoniacal nitrogen for the volume of 30 cc.

The numbers obtained by the Kjeldahl method in general, were lower than those obtained by the soda-lime method when no stearic or benzoic acid is used. The numbers obtained when stearic acid alone was used were sometimes inferior to those obtained by the soda-lime method. The numbers obtained when benzoic acid was used were, in general, about the same as those obtained by the soda-lime method.—*Muller, Annales de Chimie et de Physique, March 1891, pp. 393 et seq.* H. W. W.

NOTE.—It would seem that the double distillation, outlined above for the Kjeldahl method, would not be necessary if due care were exercised in the first distillation.

In the soda-lime method time would be saved by the reception of the ammonia in standard acid and its titration in the usual way, unless the author expects a further decomposition of the nitrogenous products of the combustion by the final distillation.

PURIFICATION OF FACTORY AND SEWAGE WATERS.

It has long been known that ferric sulphate is a most excellent material for the purification of factory and sewage waters. The only reason why it has not come into more general use is on account of its high price. The authors describe a method of preparing it from the waste pyrites of sulphuric acid factories. If the roasted pyrites are sprayed with sulphuric acid of 66° Baumé in such a way as to form a thick paste, and the whole mass kept at a temperature of from 100 to 150 degrees for several hours, the particles of pyrites become covered with a whitish coating of ferric sulphate.

When the mass becomes gradually dry and pulverulent, it is found that the acid has almost completely saturated the particles. It is only necessary then to treat the mass with the proper amount of water to obtain ferric sulphate of any degree of concentration desired. With methodical treatment, the whole of the pyrites is converted into ferric sulphate.

Experiments made with this sulphate upon factory and sewage waters show that they become clear and transparent when thus treated in the ordinary way with lime. The expense of the treatment is also no greater. Where waters have been treated from fat factories, the whole washings of the factory are precipi-

tated with ferric sulphate, collected, and the fat extracted with bisulphide of carbon or other solvent, or by other methods.—*A. & P. Buisine, Comptes Rendus, Vol. 112, No. 16, p. 875.* H. W. W.

ESTIMATION OF PHOSPHORIC ACID IN BASIC SLAGS.

The method used by Oliveri is carried out as indicated in the following description: A weighed quantity of the slag is reduced to a fine powder. To five (5) gms. of the sample are added three times its weight of chlorate of potash and the whole is intimately mixed. The mixture is then placed in a porcelain dish and hydrochloric acid is added, little by little, until the potash is completely decomposed. Evaporation is then carried on until the mass is dry. The material is then treated with fuming nitric acid and the determination of the phosphorus is made by the ordinary gravimetric method. This is accomplished by taking the liquid portion of the solution and precipitating the phosphoric acid as ammonium magnesian phosphate. After washing, it is finally weighed as pyrophosphate of magnesia.

By carrying on the operation as described above a reduction of phosphoric acid is avoided and the presence of an abundant quantity of potash prevents the formation of basic phosphate of iron which is insoluble in nitric acid.—*V. Oliveri, Le Stazioni Sperimentali Agrarie Italiane, Février, 1891.* H. W. W.

THE EMPLOYMENT OF PHENYLHYDRAZINE IN THE ESTIMATION OF SUGARS.

The action of phenylhydrazine upon reducing sugars, discovered some year or two ago by Fischer, offers the only known means of precipitating these bodies from solutions where they are found mixed with other substances. The osazones which are thus obtained are usually very slightly soluble in the ordinary reagents, from which fact it is easy to obtain them pure when there is at the disposition of the analyst a sufficient quantity of the material. But if the sugar to be studied is rare and if it contains, moreover, several distinct reducing bodies, the research is more delicate. It is easy then to confound several osazones which have almost identical points of fusion; for example glucosazone with galacto-

sazone. Finally it becomes impossible by the employment of phenylhydrazine to distinguish glucose or mannose from levulose alone or mixed with its isomers. Indeed, these 3 sugars give with the acetate of phenylhydrazine the same phenylglucosazone which melts at about 205° . It is noticed that the weights of osazones which are precipitated when different sugars are heated for the same time with the same quantity of the phenylhydrazine, vary within extremely wide limits. It is constant for each kind of sugar if the conditions under which the precipitation is made are rigorously the same. There is then, in the weight of the osazones produced a new characteristic of particular value. The following numbers have been obtained by heating for 1 hour at 100° one gm. of sugar with 100 cc. of water and 5 cc. of a solution containing 40 gms. of phenylhydrazine and 40 gms. of acetic acid per hundred. After cooling the liquid the osazones were received upon a weighed filter, washed with 100 cc. of water, dried at 110° and weighed. The weights of osazones obtained are given in the following table :

Character of the Sugar.	Weight of the Osazones.
Sorbine, crystallized	0.82
Levulose, "	0.70
Xylose, "	0.40
Glucose, anhydrous	0.32
Arabinose, crystallized	0.27
Galactose, "	0.23
Rhamnose, "	0.15
Lactose, "	0.11
Maltose, "	0.11

With solutions twice as dilute as those above, the difference is still more noticeable, and the different sugars arrange themselves in the same order with the exception of levulose which shows a slight advantage over sorbine and acquires the first rank. From the above determinations it is shown that levulose and sorbine give vastly greater quantities of osazones under given conditions than the other reducing sugars. It would be easy therefore to distinguish them by this reaction and to recognize their presence also even in very complex mixtures where the polarimetric examination alone would furnish only uncertain indications.

It is remarkable that these two sugars are the only ones among

the isomers or the homologues of glucose, actually known, which possesses the functions of an acetone. They are not, however, easily confounded, since the glucosazone forms beautiful needles which are ordinarily visible to the naked eye, while the sorbinosazone is still oily and when heated never gives perfectly distinct crystals.

This method also enables us to distinguish between glucose and galactose of which the osazone is well crystalized and melts at almost the same temperature as the phenylglucosazone. Finally it is observed that the reducing sugars give less of osazones than the sugars which are not capable of hydrolysis and consequently differ in their inversion products. It is specially noticed in this study of the polyglucoses (bioses, trioses of Scheibler) that this new method of employing phenylhydrazine appears very advantageous. It is sufficient to compare the weights of the osazones to that which is given under the same conditions by a known glucose, in order to have a very certain verification of the probabilities of the result of the chemical or optical examination of the mixture which is under study. All the polyglucoses which have been examined from this point of view give very decided results. The numbers which follow have reference to 1 gm. of sugar completely inverted by dilute sulphuric acid, dissolved in 100 cc. of water and treated with 2 gms. of phenylhydrazine, the same quantity of acetic acid and 5 gms. of crystallized acetate of sodium. All these solutions have been compared with the artificial mixtures and corresponding glucoses with the same quantities of the same reagents. The following are the results of the examination :

Character of the Sugar.	Weight of the Osazones.
1. { Saccharose, ordinary	0.71
{ Glucose and levulose (.526 gm. each)	0.73
2. { Maltose	0.55
{ Glucose (.052 gm.)	0.58
3. { Raffinose, Crystallized	0.48
{ Levulose, glucose and galactose, (.303 gm. each)	0.53
4. { Lactose, crystallized	0.38
{ Glucose and galactose, (.500 gm. each)	0.39

It is noticed that the agreement for each saccharose is as satisfactory as possible. Numbers obtained with the products of inversion are always a little low by reason of the destructive action

of sulphuric acid and in particular upon levulose. This is moreover quite sensible when the product has to be heated for a long time with sulphuric acid in order to secure a complete inversion. —*M. Maquenne, Comptes Rendus, Vol. 112, No. 15, Page 799.*

H. W. W.

THE GLASER OR ALCOHOL METHOD FOR DETERMINATION OF IRON AND ALUMINA IN PHOSPHATES.

The author gives details of the method, introducing modifications which meet objections brought against this method in England. $2\frac{1}{2}$ gms. of the phosphate are dissolved in 10 cc. hydrochloric acid, evaporated to dryness, taken up with hydrochloric, raised to boiling, washed out into a 250-cc. flask with as little water as possible. 10 cc. concentrated sulphuric acid are now added, and the solution is allowed to stand for five minutes, with frequent shaking. 95 per cent. alcohol is now added, the mixture is cooled, made up to the mark with alcohol, and well shaken. After the contraction in volume which takes place, it is again made up to 250 cc. and mixed. After standing one hour, it is filtered, and 200 cc. (= 2 gms. phosphate) are taken and gently evaporated to a small bulk. When organic matter is present, it is desirable to evaporate to pastiness, that the acid may partially decompose it. The solution is now washed into a beaker with about 50 to 100 cc. water, boiled for a short time with bromine or other oxidizing agent, and after adding ammonia, it is again boiled for about half an hour, cooled, a little more ammonia is added, filtered, washed with a hot solution of ammonium chloride, ignited, and weighed. The ammonium chloride is used to prevent the precipitate from washing through the filter. The phosphoric acid is determined by dissolving the ignited precipitate in acid, and the oxide of iron and alumina obtained by difference. Messrs. Teschemacher and Smith add the postscript that when magnesia is present, the phosphates of iron and alumina obtained as above must be freed from this impurity by washing the precipitate off the filter, and boiling with water and a little nitrate of ammonium.—*H. H. B. Shepherd, Chem. News 63, 251.*

A. H. W.

SEPARATION OF TIN AND TITANIUM.

The method is as follows: The ore containing tin oxide and titanitic acid is put into a dry tube of combustion glass and ignited in a current of hydrogen for about fifteen minutes over a common Bunsen burner. After cooling in the current of hydrogen, the gray mass is rinsed into a beaker with water, and any small portions adhering to the sides of the tubes are dissolved by treating with dilute hydrochloric acid and afterwards rinsing with water. 30 cc. of 20 per cent. hydrochloric acid are now added, and the solution is boiled for half an hour, gently cooled, filtered, and the residue is washed with water. After neutralizing, and slightly acidifying, a current of sulphuretted hydrogen is passed into the filtrate, and the tin sulphide thus precipitated is collected, washed with water containing a little ammonium acetate, and dried. After incinerating the filter paper, the tin sulphide and ash of the filter are reduced by ignition in a current of hydrogen. The reduced tin is washed with water and a little dilute nitric acid into a capacious porcelain crucible, 10 cc. of dilute nitric acid are added, when the solution is evaporated to dryness on the water bath. The residue is taken up with nitric acid and hot water, and the tin oxide determined in the usual way. According to the author, the tin sulphide may be also reduced in a weighed tube and weighed as metal. The titanitic acid in the residue is burnt with the filter paper and melted in a platinum crucible with 10 parts of potassium carbonate. The fusion is dissolved in about 200 cc. of water, to which concentrated sulphuric acid is added, drop by drop, till the acid potassium titanate dissolves. The solution is neutralized with sodium carbonate, 2 gms. of conc. sulphuric acid are added, the solution is diluted to 400 cc. with water, and boiled for six hours, replacing the water as it evaporates. On account of the "bumping," this part of the operation is best conducted in a large, well glazed porcelain dish, covered with a clock glass or inverted funnel. After filtering off the titanitic acid, the filtrate is measured, mixed with enough sulphuric acid so that there may be 0.5 per cent. in the liquid, and boiled. Any more rarely separates out. The titanitic acid is dried, ignited and weighed. In case of ores containing silicates, the silica is removed by evaporating down with hydrofluoric acid. In presence of a

ferric salt, Haas separates the titanitic acid exactly according to Levy's instructions, filters off the ferriferous titanitic acid, ignites in a current of hydrogen in a glass tube, rinses out the reduced mass, boils for half an hour with 20 per cent. hydrochloric acid in a beaker, and weighs the white residue as pure titanitic acid.—*H. Haas, Chem. News* **63**, 195. (*Zeitschrift für anal. Chemie.*)

A. H. W.

A CURIOUS PROPERTY OF SULPHUR.

In demonstrating that sulphur, melted at about 115 degrees, can be cooled in paper, the author happened to use a lithographed card of which the edges were turned up. Upon taking away the card he discovered that the lithographed characters were clearly and distinctly impressed upon the cooled surface of the sulphur, and remained after hard friction and washing. By repeated experiments he has been able to get very fine results, removing the paper each time by a mere washing and rubbing process. He finds that sulphur will receive impressions from and reproduce faithfully characters or designs in ordinary graphite crayon, colored crayons, writing-ink, typographical inks, china ink, lithographic inks—colored or uncolored, and others. He remarks, too, that it will reproduce with remarkable exactitude geographical maps.—*M. Charles Lepierre, Bull. Soc. Chim.* **5**, 308. W. W. D.

A REACTION OF CARBONIC OXIDE.

The author has found that this gas will reduce silver nitrate in cold ammoniacal solution. Upon boiling, a heavy black precipitate occurs. This reaction will work equally well with an aqueous solution of the gas. It is extremely sensitive, and takes place even in the presence of a great quantity of air. On this account, it will be useful in determining the presence of small traces of carbonic oxide in a gaseous atmosphere, provided it contains no other reducing agent. The reaction is the more worthy of interest on account of the fact that neither the alkaline formates, nor pure hydrogen, after it has been washed with potassium permanganate solution, will reduce ammoniacal silver nitrate.—*M. Berthelot, Bull. Soc. Chim.* **5**, 569.

W. W. D.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
PURDUE UNIVERSITY.]

II. THE QUANTITATIVE DETERMINATION OF FURFUROL AND THE PENTOSE CARBOHYDRATES.

BY W. R. STONE.

The aldehyde, *furfural*, on account of its unusually reactive nature, has been the subject of much study, and its derivatives have been very thoroughly investigated. Of late it has gained new interest from the discovery that it is a characteristic decomposition product of the *pentoses* or, primarily, of those gum-like bodies from which they are derived. These bodies, as they naturally occur, are undoubtedly the source of furfurol, as it is obtained by the usual methods of destructive distillation. Therefore, the production of furfurol in this way has come to be regarded as a characteristic reaction for the occurrence in vegetable materials of those complex bodies from which the pentoses are derived,* and which we may consistently designate as *pentosans*.† On this basis I have lately pointed out that these bodies are widely diffused in nature, by preparing from a considerable number of crude materials, appreciable quantities of furfurol.‡ Elsewhere§ I have called attention to the fact that the presence of these bodies in many materials used for food, must have a misleading influence upon our interpretation of food analyses, since the *pentosans* respond to most of the reactions for carbohydrates, and are ordinarily

*Annalen der Chemie (Liebig) 249, 227.

†The term *pentan*, lately proposed by me for this class of bodies, is easily confused with *pentane*, as applied to the hydrocarbons C_5H_{12} . "Pentosan" will, therefore, be a less confusing and equally expressive term.

‡Am. Chem. Jour. 13, 73; Ber. d. d. chem. Gesell. 23, 3791.

§Agricultural Science 5, 91.

placed to their account, while differing from them in physiological and analytical values. It is evident, therefore, that some method by which this class of pseudo-carbohydrates can be recognized, and if possible, quantitatively estimated as they occur in nature, accompanying the true carbohydrates, is an essential condition to their farther study in this direction.

Two such methods have been proposed by Tollens and his pupils.* Simultaneously I have also been engaged upon the same subject, and because the method which I propose differs essentially from those mentioned, I present it here somewhat in detail.

All methods thus far proposed are based upon two operations : first, the production of furfural from the pentosans contained in a known quantity of the material under examination ; second, the quantitative estimation of the furfural thus obtained.

The original process by which Dobereiner obtained furfural was by distilling wheat-bran with strong sulphuric acid and manganese dioxide.† Stenhouse found the use of the latter unnecessary ;‡ by distilling equal weight parts of bran, sulphuric acid and water, he obtained from 12 lbs. of bran, one ounce of furfural. (By the improved method 13 ounces are obtained from the same amount of material.) By using one-half as much acid and water, Fownes obtained one ounce of furfural from five pounds of bran.§ Babo obtained furfural by distilling bran with zinc chloride.||

The general method followed in the manufacture of furfural has been to distill bran with one weight part of strong sulphuric acid and three weight parts of water until about three-fourths of the liquid has passed over, the furfural being found in the distillate. By this method the weight of the crude furfural obtained is about three per cent. of that of the bran employed.

As soon as attention was directed to the *source* of the furfural thus obtained, attempts were made to perfect this crude and destructive method. In the original investigations¶ which characterized furfural as a specific derivative of the pentoses and pento-

*Tollens and Günther, Ber. d. d. chem. Gesell. 23, 1751; Tollens and de Chalmot, Ibid 24, 694.

†Berzelius' Jahresbericht 21, 328.

‡Ann. der Pharm. 35, 301.

§Liebig's Jahresbericht, 1847-1848, 731.

¶Ann. Chem. Pharm. 85, 100.

¶Annalen d. Chemie (Liebig) 249, 227, and 254, 304.

sans, 5 gms. of material were distilled with 10 cc. of strong sulphuric acid and 30 cc. of water, replacing the loss by distillation with water, as long as any furfurol passed over. In this way fairly constant, but as it now seems, too low results were obtained. Allen and Tollens* found that the formation of furfurol occurred more regularly and with fewer variations if hydrochloric were substituted for sulphuric acid, and this was further emphasized in the quantitative method proposed by Tollens and Günther.† Finally Tollens and de Chalmot have decided that the use of hydrochloric acid of 1.06 sp. gr. produces the best results.‡

These methods all necessitate the slow distillation of the material with some reagent, a time-consuming operation, to avoid which I have sought other means of accomplishing the same end, with, however, only negative results. By treating various substances, known to contain the pentosans, with acids (sulphuric and hydrochloric) of various concentrations during longer or shorter times, in connection with an inverted condenser, I was able to prove, that either the action of the acids was not sufficient to effect a complete transformation of pentosans into furfurol, or, if strong enough for this, the furfurol produced itself underwent destruction. Similar tests, made in sealed flasks under pressure, led to the same results. The agent producing the furfurol seems also capable of destroying it when the action is long continued. Hence there are at present no better methods of obtaining furfurol than those which provide for its continuous removal by distillation from contact with the producing agent.

Other reagents have also been used in this connection, viz., zinc chloride, calcium chloride with hydrochloric acid, etc. With the former the results were no better than with sulphuric acid; with the latter, somewhat higher. None of these processes, however, yield so good results as the distillation with hydrochloric acid as proposed by Tollens and de Chalmot. This I have carried out as follows:

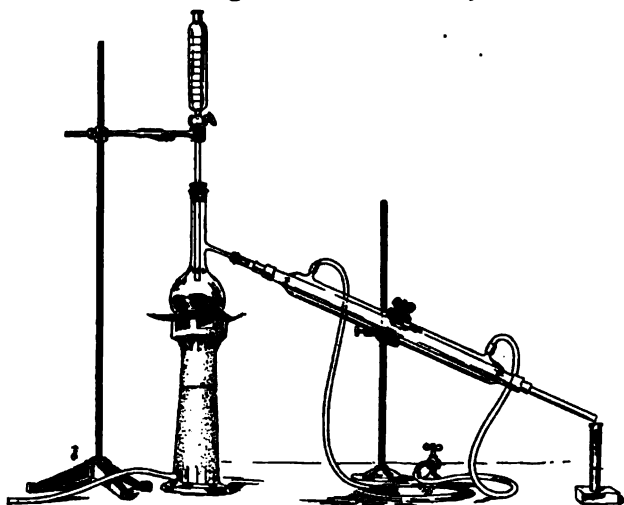
2 to 5 gms. of the material, finely ground as for the ordinary fodder analysis, are placed in a distilling flask with 100 cc. of hydrochloric acid, sp. gr. 1.06. The mixture is then distilled,

*Ber. d. d. chem. Gesell. 23, 137.

†Ber. d. d. chem. Gesell. 23, 1751.

‡Ibid, 24, 694.

and the distillate collected in a graduated receiver. As soon as 10 cc. have distilled off, the loss is replaced by 10 cc. of acid of the same strength, run in from a graduated stoppered funnel. This process is repeated until the drops of distillate no longer give the characteristic red color on filter paper moistened with anilin acetate.* The apparatus used successfully by me is shown in the cut. The distilling flask is an ordinary fractionating flask



of 200 cc. capacity. The stoppered funnel for replacing the distillate holds 100 cc., and is graduated to 10 cc. The receiver is a test tube divided into 10 cc. portions. Tollens and de Chalmot place the distilling flask in a bath of Rose's metal. A paraffin or oil bath may serve the same purpose. I have dispensed with the bath and heat the distilling flask on a wire gauze, taking care to regulate the flame so that fully five minutes are required for the distillation of 10 cc. In this way the distillation of an ordinary material occupies about two hours, the volume of the distillate attaining 200 to 250 cc. The small 10 cc. portions of the distillate are collected in a roomy flask containing solid sodium carbonate for the neutralization of the free acids. At the close of the operation a slight excess of acetic acid is added, the solution filtered if

*This reaction is very sensitive. One drop of a solution of one part furfural in 100,000 parts of water gives a brilliant red color upon paper moistened with a mixture of equal parts of glacial acetic acid and anilin.

necessary, made up to a definite volume, and is ready for the second part of the determination. The solution now contains all of the furfurol, together with the sodium salts of the hydrochloric and small quantities of organic acids and traces of undetermined organic products.

For the determination of the furfurol in this distillate, the characteristic reactions of the same may be made use of. Of these, two, or possibly three, are distinguished for their sensitiveness. H. Schiff has shown that furfurol combines with the aromatic bases, forming chromogens, which however yield mostly only temporary or fugitive colors.* Of these reactions, that with anilin† is particularly sensitive, as already pointed out in its use during the distillation. This in itself, however, has been used only as a qualitative reagent. Schiff‡ states that xylidin acetate is still more sensitive, but I have not found it so.

The most permanent form into which the furfurol can be readily converted is the ammonia compound or the furfuramid,§ (C_5H_4O), N ,(C_5H_4O), N . This reaction is the one made use of in most of the researches thus far published upon the pentoses and pentosans. It involves the concentration of the furfurol containing distillate by a tedious fractional distillation, precipitation with ammonia, and eventual weighing of the furfuramid. The objections to the method are, the time required for the operation and the solubility of the furfuramid, preventing complete precipitation. Moreover, in anything less than a saturated solution of furfurol, ammonia will produce no precipitate. Hence, this method fails by a considerable error to indicate the entire amount of furfurol.

E. Fischer's reagent for aldehydes and ketones in general, phenylhydrazin, is particularly sensitive toward furfurol.|| He characterizes it as the most convenient and sure reagent for the recognition of small quantities of furfurol. A dilute phenylhydrazin solution produces a distinct reaction in a solution of one part furfurol in 10,000 parts of water. Tollens and Günther made

**Annalen der Chemie* (Liebig) 201, 355, and 239. 349.

†*Stenhouse*, *Ibid.* 74, 282.

‡*Ber. d. d. chem. Gesell.* 20, 540.

§*Fownes*, *Annalen der Chemie* (Liebig) 54, 52, and R. Schiff, *Ber. d. d. chem. Gesell.* 10, 1188.

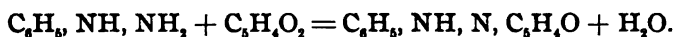
||*Ber. d. d. chem. Gesell.* 17, 574

use of this reaction in the earlier method proposed for the estimation of furfural.* In brief, they titrated the furfural solution with a standard solution of phenylhydrazin, using the anilin acetate reaction to indicate the point when no more furfural remained uncombined. This indicator is not reliable, however, and for this method Tollens and de Chalmot have since substituted another,† based upon the separation and weighing of the furfuralhydrazon. Here, as in the case of the furfuramid, the precipitation is not complete, a certain amount remaining in solution, for which a correction of .0252 gm. is made. In this respect this method has little advantage over the precipitation as furfuramid.

The method proposed by me is a volumetric one, involving the titration of the dilute furfural solution with a dilute solution of phenylhydrazin of known strength indicating the point at which an excess of the latter has been added by its delicate reaction with Fehling's solution.

The preparation of the distillate has already been described. It should contain a slight excess of free acetic acid. Small aliquot parts are taken, usually 25 cc.

The standard solution of phenylhydrazin is prepared by dissolving 1 gm. of the chloride with 3 gms. of sodium acetate in water, and diluting to a volume of 500 cc. Such a solution contains 0.747 gms. of phenylhydrazin, or in 1 cc. 0.001494 gm., which is theoretically equivalent to 0.001328 gm. of furfural, according to the reaction



The solution is standardized by titrating against a solution of furfural of known strength, prepared as follows: The crude commercial furfural is purified by digestion with dilute sulphuric acid and dichromate of potassium, and eventually by fractional distillation; it is then precipitated by ammonia, and this preparation recrystallized from alcohol, and finally dried over sulphuric acid. 1 gm. of this is equivalent to 1.0746 gm. of furfural. The standard solution is prepared by dissolving 1 gm. of this furfuramid in dilute acetic acid, and diluting to a volume of one liter, each cc. of which then contains 0.0010746 gm. furfural. By repeated trials

*Loc. cit.

†Loc. cit.

10 cc. of this solution required 15 cc. of the phenylhydrazin for complete combination,—*i. e.*, the value of 1 cc. of the phenylhydrazin solution is 0.0007164 gm. of furfural. The phenylhydrazin solution is unstable, and should be freshly prepared after twenty-four hours, although when kept in a dark cool place it has been known to retain its number three days. Attempts to prepare a more stable solution by addition of alcohol, acetic acid, etc., were without satisfactory results.

The titration is carried out as follows: 25 cc. of the furfural containing distillate already described, contained in a four-ounce Erlenmeyer flask, receive 25 cc. of water and a certain quantity of the phenylhydrazin solution run in from a burette. The flask and contents are placed on a gauze over a flame and quickly brought to the boiling temperature. If much furfural be present, the liquid quickly becomes turbid and of a pale yellow color. As soon as ebullition occurs, the flask is cooled by immersion in cold water. The liquid now becomes densely opaque, and the color deepens to a bright orange red, caused by the formation of the finely divided amorphous or scaly furfuralhydrazon. When thoroughly cool, a portion of the liquid is filtered. The filtrate should be perfectly clear and of a pale golden yellow color; if not so, or if it becomes turbid on standing a few seconds, it should be refiltered until this stage is reached. 2 cc. of this filtrate placed in a test tube receive 4 cc. of freshly mixed Fehling's solution, thoroughly shaken, and quickly heated to boiling. If the least excess of phenylhydrazin has been added, the mixture turns a greenish yellow, even before the boiling point is reached. If the furfural is still in excess, the dark blue color of the Fehling's solution remains unchanged. This part of the reaction is very delicate, the contrast between the unchanged Fehling's solution and a very slight reduction of the same is very apparent, even at some distance, when viewed by reflected light.* *This change of color preceding or during the boiling, fixes the reaction.* A subsequent change on standing is not regarded. If too little or too much of the phenylhydrazin has been added the first time, more or less is run in on a second trial, and this repeated until the exact number

*The reduction of Fehling's solution by phenylhydrazin is very marked. One part of the latter in 55,000 parts of water reduces Fehling's solution distinctly *in the cold* when mixed in equal volumes.

is determined. This part of the manipulation is similar to that followed by many in the titration of invert sugars with Fehling's solution, as an example will best illustrate. In a preliminary test, 15 cc. of the phenylhydrazin solution are too much; in the second trial, under precisely the same conditions, 13 cc. are used and found to be too little; a third trial shows 14 cc. to be too much; 13.5 cc. is too little; 13.8 cc. is also too little, which fixes the number at 13.9 cc., which may then be confirmed by the sixth trial.

Working with solutions of the dilution specified, an excess of one-tenth cc. of the phenylhydrazin is sharply recognized. Indeed, unless great attention be given to details, the errors of manipulation will easily lead to confusion. If the conditions are strictly observed, the results are wholly concurrent. An error of one- or two-tenths cc. in the titration makes, however, little difference in the result, as the following example will show:

2.5 gms. of material were distilled, and the distillate made up to a volume of 400 cc. 25 cc. of this required 10 cc. of the phenylhydrazin solution indicating .007164 gm. of furfurol, or in the entire amount .114624 gm. furfurol, or 4.584 per cent., calculated to the original material. If 10.1 cc. of the phenylhydrazin solution had been used, the result would have been 4.631 per cent., or a difference of .047 of one per cent., under conditions in which the error is greatly multiplied.

The method, as described, seems somewhat complicated, but in practice is not more so than the ordinary titration of a sugar solution, and is capable of quite as accurate results. The chief source of error lies in the distillation by which the furfurol is produced. In this part of the operation, it is easy, as I have indicated, to destroy the furfurol or to cause too rapid destruction of the material before giving time for the formation of the furfurol. This can only act, however, to give too low results. The determination of the furfurol itself I believe to be highly accurate.

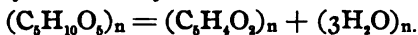
Following are some results obtained by this method, some of which are data in an investigation concerning the digestibility of the *pentosans*, a study rendered possible only by means of the quantitative method here described. The distillations were made in duplicate from 2.5 gms. of material in each case.

Gum prepared from corn cobs . .	{ a. 51.88	per cent. furfural	
	{ b. 48.66	" "	
Wheat bran	{ a. 6.83	" "	
	{ b. 7.16	" "	
Bran and meal mixed	{ a. 4.61	" "	
	{ b. 4.64	" "	
Rabbit dung (1)	{ a. 7.99	" "	
	{ b. 8.30	" "	
Rabbit dung (2)	{ a. 7.76	" "	
	{ b. 8.62	" "	
Rabbit dung (3)	{ a. 10.59	" "	
	{ b. 10.04	" "	

The application of this method to the examination of vegetable materials, foods, feeding stuffs, etc., for the relative occurrence in them of the pentosans, remains to be pointed out. The amount of furfural obtained represents a certain amount of pentosans in the original material, but in just what proportion is not well understood. All experience seems to indicate that the gum-like pentosan is a complex body of high molecular weight, which possibly bears some such relation to the pentoses (arabinose or xylose, as the case may be) as starch does to dextrose. The first action of the acid during the distillation is, doubtless, to break up this molecule into pentoses. If this action is hydrolytic, then the weight of the resulting pentoses is greater than the pentosans according to this reaction.



The continued action of the acid then converts the pentoses into furfural probably in this way.



According to these reactions, therefore, the furfural obtained stands in relation to the pentosan from which it is derived, of 1 to 1.381. There are no data, however, on which to base the above reactions, although analogy indicates something of the kind. The actual amount of furfural obtained is doubtless always less than the theoretical, owing to the destructive nature of the process employed. The method here proposed is, therefore, not absolute, but comparative, and only from this standpoint possesses direct value.

I need only refer to the results given here and in other related papers to illustrate the application of this method for the comparative estimation of the pentosans and the importance of these bodies as food constituents.

DETERMINATION OF MANGANESE IN MANGANIFEROUS SLAGS AND ORES.

BY G. L. NORRIS, PENCOLD, PA.

The manganese in slags from blast furnaces making spiegel, and in open hearth slags, is easily and rapidly determined in the following way.

1 gram of the finely powdered slag is placed in a 4 oz. Griffin beaker, moistened slightly with water, to prevent caking, and 50 cc. of nitric acid of 1.42 sp. gr. added. Bring to a boil, and while the slag is in suspension, add 3 or 4 cc. of hydrofluoric acid. The slag is rapidly decomposed and the silica driven off. Boil the solution for a few minutes, to drive off any remaining hydrofluoric acid, then transfer to a larger beaker, or a precipitating flask, add more nitric acid, bring the solution to a boil, and precipitate the manganese with potassium chlorate. Filter off the manganese dioxide upon an asbestos filter. The manganese dioxide may either be dissolved in standardized oxalic acid, or ferrous sulphate solution, and the excess of the solvent titrated with permanganate of potassium, and the amount of manganese calculated; or the manganese may be finally weighed as the pyrophosphate.

For manganese in ores: 1 gram or .5 gram according to richness of the ore, is placed in a 4 oz. Griffin beaker, moistened with water and 50 cc. nitric acid of 1.42 sp. gr. added. Bring to a boil and add a few small pieces of tartaric acid. Ores made up largely of the mixed oxides of manganese go into solution readily. When the solution clears, add a little hydrofluoric acid to decompose the residue. Where there is much oxide of iron in the ores, it is better to add the hydrofluoric acid along with the tartaric acid.

Drive off any remaining hydrofluoric acid and be sure that the tartaric acid is all decomposed. Add more nitric acid, boil, and precipitate the manganese with potassium chlorate.

The nitric acid breaks up all the other oxides of manganese, into the oxide and dioxide and dissolves the monoxide, while the tartaric acid causes the solution of the dioxide. Considerable tartaric acid may be used as it is readily decomposed by boiling in the nitric acid solution.

By this method the manganese can be determined in about 45 minutes, while a much longer time is required by the ordinary way of solution in hydrochloric acid, with separation and fusion of the residue and consequent accumulation of salts.

COMPOSITE MILK-SAMPLES IN THE LABORATORY.

BY G. E. PATRICK.

Composite milk-samples for use at creameries, as a means of saving labor in the valuing of milk by any of the "oil tests," I first proposed (in detail) in Bulletin No. 9, of the Iowa Experiment Station, May 1890. The preserving agent there recommended for preserving the samples was corrosive sublimate, HgCl_2 , numerous experiments having shown that it preserves the *mechanical*, as well as the chemical, condition of milk better than any other common antiseptic. For use in creameries I insisted that the sublimate have mixed with it some suitable aniline color, as a guard against accidental poisoning; and to hasten solution in the milk, admixture of common salt, NaCl , was recommended.

For six months past I have employed the same principle in the laboratory, in analyzing the milk of experimental cows, not only for fat (by one of the "oil tests") but also for solids, gravimetrically. (See Iowa Station Bulletin No. 13, page 29, May 1891).

For this purpose the preservative is of course used without admixture of aniline color or common salt, as these would bring error in the results on solids.

The corrosive sublimate is powdered finely and passed through a very fine gauze sieve. Only a very small amount is needed to preserve milk-samples five or six days without material change; and five days is as long as such keeping is desirable in most experiments on milk production. For keeping five days, .125 gm. of the HgCl_2 is sufficient in cool weather, and .200 gm. in summer weather, provided the daily samples are 50 cc. each, making the complete composite sample 250 cc. The theoretical error thus introduced in the result on solids is only .05 per cent. with the smaller amount, and .08 per cent. with the larger; the former figure is within the "limits of error" in ordinary routine work, and the latter nearly so, if not quite. Many comparative trials have, however, convinced me that there is a *very slight* loss in the solids of milk preserved for five or six days, but that it rarely exceeds .05 per cent.; therefore it is my custom to neglect correction for the HgCl_2 when it amounts to only .05 per cent.; and when it amounts to .08 per cent. to correct by deducting .03 per cent. These corrections are accurate enough for use in routine

work, by the method of drying in air on fine asbestos in open watch-glasses—the method which I have thus far employed; doubtless finer work could have been done, and perhaps more accurate corrections found, by the method of drying in hydrogen, had time permitted the employment of this method.

The following test determinations were made by Mr. E. N. Eaton, assistant chemist in this station.

1. Experiments in which the entire sample of milk was preserved for the time named—no daily additions of fresh milk having been made.

(a.) With .05 per cent. of HgCl_2 added; no correction is made for this in final results.

	Solids in Fresh Milk.	No. of Days Preserved.	Solids in Preserved Milk.
Sample No. 1.	10.34	5	10.34
" " 2.	12.35	5	12.45
" " 3.	10.95	5	10.92
" " 4.	11.13	5	11.13

(b.) With .10 per cent. of HgCl_2 added: results corrected by deducting .05 per cent.

	Fresh.	No. of Days.	Preserved.
Sample No. 5.	11.27	8	11.27—.05=11.22 per cent.
" " 5.	"	9	11.33—.05=11.28 per cent.

(c.) With .65 per cent. HgCl_2 added, by mistake; results corrected by deducting .60 per cent.

	Fresh.	No of Days.	Preserved.
Sample No. 6.	13.47	8	13.94—.60=13.34 per cent.
" " 6.	"	9	14.06—.60=13.46 per cent.

This last trial (c) indicates that the usual amount of HgCl_2 , viz: .05 per cent. is as efficient as a much larger quantity.

2. Composite samples; fresh milk added each day; HgCl_2 added=.05 per cent. on entire composite sample. Results not corrected.

	Mean of Results on Daily Samples Analyzed Separately.	No. of Days.	On Composite Samples.
Cow 114.	10.53	5	10.45
" 115.	10.80	5	10.78
" 37.	14.30	5	14.36
" 38.	14.60	5	14.58

In warm weather I prefer the use of .08 per cent or .10 per cent. of HgCl_2 , with a correction of .03 or .05 per cent.

Lightning or Mason jars are convenient receptacles for the composite samples. The mercuric chloride is weighed out and placed in the jar at the time of adding the first daily sample, or before. Upon the addition of each daily sample to the composite, the latter should be well mixed by a rotary motion—not by shaking—in order to redistribute the cream throughout the whole; and this mixing should be done every day, whether the samples be added every day or not.

Sometimes, especially in warm weather, the composite sample will have floating upon its surface small flecks of milk-solids; these can be broken up, and the sample brought into almost perfect mechanical condition, by means of a stiff test-tube brush used as a pestle inside the jar, rubbing the flecks to pieces against the walls of the latter.

One must guard against error from the rising of minute flecks of milk-solids to the surface while weighing out the charge; this is easily done by inverting the weighing pipette once or twice just before running out the charge upon the asbestos.

It hardly needs saying that in summer the composite samples should be kept in as cool a place as possible; ice or cold water would of course be useful.

EXPERIMENT STATION, AMES, IOWA.
AUGUST 10, 1891.

A METHOD OF OBTAINING AMMONIA-FREE WATER.

By D. B. BISBEE.

A very easy way of obtaining ammonia-free water, which I have used for some time and have never seen mentioned, is to acidulate the water, before distilling, with sulphuric acid. The acid holds all ammonia in the retort, the first portions, even, of the distillate being ammonia-free. But this acidulation naturally causes the nitric and nitrous acids in the water to distill over. For some purposes, however, nitrates are not objectionable. At this laboratory, when we wish to obtain chemically pure water for any use, we take distilled water, which is nitrate-free, acidulate with sulphuric acid and distill, at once getting *pure* water.

IOWA AGRICULTURAL EXPERIMENT STATION,
AMES, IOWA, July, 1891.

A NEW DISTILLING FLASK FOR USE IN THE KJELDAHL PROCESS.

BY G. E. PATRICK AND D. B. BISBEE.

The only serious drawback to the Kjeldahl method of nitrogen determination is the breakage of distilling flasks, and in laboratories where many determinations of albuminoid nitrogen are made by the Stutzer process, this breakage is often a matter of much annoyance and considerable expense, since only the best quality of flasks will long stand the requirements of the process.

Some months ago the breakage in a certain lot of flasks purchased for this laboratory having become unendurable, the writers hit upon the idea of distilling from copper flasks; and upon trial, the results have been so satisfactory that we can with confidence recommend the plan to other chemists. The copper flask used was the ordinary one-pint oxygen retort minus the cap, delivery tube and clamp.

At first trials were made by distilling ammonia from a solution of pure ammonium chloride and NaOH, to assure ourselves that no ammonia was retained by the copper. These results were made comparative by distilling from both glass and copper flasks. Exactly 10 cc. of an ammonium chloride solution of known strength were used in all following tests. The results, after deducting for error found by blank experiment, were as follows:

				In Glass Flasks.	In Copper Flasks.
No. of cc. of decinormal acid neutralized				14.4	14.25
" " " "				14.23	14.23
" " " "				14.2	14.30
" " " "				14.28	14.25
" " " "				14.3	14.25
" " " "				14.15	14.30
Mean of six				14.26	14.26

Next a salt of mercury was added to the ammonium salt in the flasks, and K_2S , sufficient to precipitate the mercury, was added before liberating the ammonia and distilling. The following were the results after deducting for the error of the blank.

					In Copper Flasks.
No. of cc. decinormal acid neutralized					14.13
" " " "					14.25
" " " "					14.25
" " " "					14.2
" " " "					14.25
" " " "					14.25
Mean of six					14.22

These results compare favorably with those from glass just reported.

Next, to imitate the condition of Stutzer's process, copper hydrate, as well as a mercuric salt and K_2S , was added. Results, after deducting the blank, were as follows :

					In Copper Flasks.
No. of cc. of decinormal acid neutralized					14.2
" " " " "					14.2
" " " " "					14.3
" " " " "					14.25
" " " " "					14.25
Mean of five					14.24

Here, again, the results were practically identical with those obtained by distilling from glass.

The plan was then tried upon the product of the Kjeldahl digestion in fodder analysis, both in total and albuminoid nitrogen determinations, the results in all cases being in substantial agreement with those obtained by distilling from glass; and now we use the metallic flasks in the regular analytical work of the laboratory. A few results will suffice to illustrate.

Substance Taken.	Results in Copper.	Results in Glass.
Shorts, total Nitrogen	2.81 per cent.	2.81 per cent.
Shorts, Albuminoid Nitrogen	2.26 "	2.26 "
Cream Gluten Meal, Total Nitrogen	6.28 "	6.27 "
" " Albuminoid " {	6.18 "	6.24 "
" " Albuminoid " {	6.21 "	6.22 "
Sugar Meal, Total Nitrogen, (Determinations made 2 months apart)	3.33 "	3.19 "

We employ 200 cc. of water in transferring the contents of the digestion flask into the distilling flask, using about half of it in diluting and cooling the acid liquid before actually transferring. We are also in the habit of introducing 30 cc. of the K_2S solution, instead of 25 cc., as is usually directed. This may not be necessary, but the fact that the residual liquid after distillation is always free from (binary) sulphur, the excess being removed by the flask itself, seems to render a little extra sulphide advisable. This action between the sulphide and the copper will doubtless in time destroy the flasks; but long before that time arrives they will have saved in glassware many times their cost.

The flasks are heated by rather small, naked flames; a large flame under the one pint flask will boil the charge over. The receiving flasks are marked at the 200 cc. level to show when the operation is finished. No zinc or pumice is required to prevent "bumping"; otherwise, the arrangements are as usual.

The distillation is completed within 30 minutes; so the saving of time is very great.

IOWA AGRICULTURAL EXPERIMENT STATION,
AMES, IOWA.

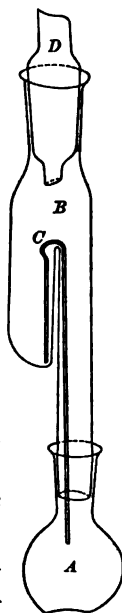
A NEW GLASS SIPHONING EXTRACTION APPARATUS.

BY J. T. WILLARD AND G. H. FAILYER.

Before describing our apparatus, a few words in justification of its invention, notwithstanding the many forms already proposed, may not be out of place. First, we are led to reject any extractor which makes cork connections. The extreme difficulty of completely freeing cork from its resinous constituents can be appreciated only by one who has extracted the properly perforated corks for one hundred hours or more in a large Soxhlet's extractor, and at the end of that time has still found appreciable quantities of extract. Then, too, the more perfectly a cork is exhausted, the less suited does it become, mechanically, for use, losing its toughness and elasticity. Second, a *siphoning* apparatus must be preferable to a percolating, because we are certain that every particle of the substance is soaked by fresh solvent every time the container is filled, while in a percolating apparatus

we can never be quite sure that the solvent is not chiefly flowing down channels of least resistance and leaving portions of the material comparatively unacted upon. Soxhlet's extractor, when made with ground joints, will doubtless give good satisfaction. The form we are about to describe has, however, the advantage of greater simplicity, and is consequently cheaper and less liable to fracture.

By reference to the cut, it will be seen that our extractor consists of four parts, viz., the *flask*, *A*, the *containing tube*, *B*, the *condensing tube*, *D*, and the *siphon*, *C*. The flask is small, holding about 100 cc., and weighing about 20 gms. The containing tube is ground into the neck of the flask, and has a pocket on one side, in which the substance, inclosed in a sack formed of fat-free filter-paper, is placed for extraction, and into which the short arm of the siphon dips. The condensing tube expands to a stopper for the containing tube, and at the lower end is drawn out and ground off in such a way as to direct the condensed solvent into the pocket containing the substance for analysis. The upper part of the condensing tube passes through a cold water jacket of some kind: ours is a copper tank large enough for six extractors. The siphon is made of small tubing, the inside diameter being about 2 mm. At the bend it must be less, but must not be constricted so much as to greatly impede the flow of the liquid through. The capillary attraction exercised by the inner wall of the siphon raises the liquid sufficiently to bring the siphon into action before the pocket is full enough to run over. The upper end of the short limb of the siphon must not be too close to the side of the pocket or the capillary action of the outside of the siphon, and the side of the pocket will draw the liquid over without filling the siphon. To prevent this, the siphon may be bent sharply away from the wall of the pocket, as shown in the cut, or the wall itself may bend away at that point. If these details be met in the construction of the siphon, it will empty the pocket promptly, and the apparatus will require no attention after the flame is adjusted under the water-bath.



The apparatus is so constructed that the siphon may be easily removed, and when the extraction is concluded, the substance and the siphon are removed and the solvent distilled up into the pocket. If too large an excess has not been taken, the removal of the siphon and the substance will give ample capacity to the pocket to receive the solvent remaining. The drying of the extract is completed in hydrogen, as usual.

The extractor, as figured, was constructed for the quantitative analysis of feeding stuffs. The containing pocket was therefore made small, to insure quick siphoning and to require but little absolute ether. It is, however, apparent, that within certain limits the apparatus might be made of considerable size. We have more recently had a number constructed especially for milk analysis. In these the containing pocket is made large enough to admit the paper coil upon which the milk is dried if Adams' method is employed, or a drying tube filled with asbestos when desiccation is effected upon that substance. These extractors are each provided with two flasks, thus doubling their efficiency and enabling one to keep them all in constant service.

Our extractors are so arranged that each set of six is heated by a single water-bath. This consists of a flat copper box. The extractors are held up in place by strong spiral brass springs. Each spring has a piece of brass gauze soldered across the upper coil. The diameter of the coil is greater than that of the bottom of the flask. The springs, while rather stiff, must be so adjusted in length as to require but little compression to bring them in position.

We have used the extraction apparatus above described in the analysis of feeding stuffs for over a year and a half with the greatest satisfaction. Fitted with two flasks, and charged with absolute ether, which is protected by a calcium chloride tube in the upper end of the condensing tube, the apparatus seems to us to leave little to be desired in simplicity or perfection of action.

[NOTE.—Mr. J. T. Crawley, in the *Am. Chem. Jour.*, Vol. XI, p. 507, has described an apparatus employing capillary attraction to bring the siphon into action. It seems right to say that our extractor was designed before the publication of his article.]

KANSAS EXPERIMENT STATION,
MANHATTAN, KANSAS,
August 10, 1891.

A METHOD OF STANDARDIZING IODINE SOLUTION FOR THE DETERMINATION OF SULPHUR IN STEEL AND PIG-IRON.

BY JO. M. WILSON.

I desire to call attention to a method of standardizing iodine solution, for use in titrating sulphur in iron and steel, which has been in use in the laboratories of some of the iron works of the Ohio Valley for the past four years, and which, I believe, I was the first to use, in the laboratory of the Laughlin & Junction Steel Co., at Mingo Junction, Ohio.

Finding the hyposulphite method would occasionally fail and frequently gave non-concordant results, on doubling quantities, I cast about for a substitute, and at length settled on a steel the sulphur contents of which had been very carefully determined by *all* the known evolution methods as a standard.

By using this standard steel I standardized my iodine solution by the same process that I used to determine the unknown percentage of sulphur in the samples of pig metal and steel submitted for analysis, avoiding the objections raised by certain chemists, that the hydrocarbons evolved with the hydrogen sulphide interfered with the titration by iodine when KOH was used as an absorbent; for the iodine solution being standardized under conditions of actual working, it is to be presumed that inasmuch as all the C in our standard steel is combined, there will be as much hydrocarbon evolved therefrom as from any sample we may have submitted to us for determination.

As to accuracy, there can be no question on that score; the only essential being that we make sure of complete solution of the metal under treatment by taking plenty of time to *complete the solution* of the *difficultly soluble sulphides, etc.*, which invariably accompany high sulphur irons, and making sure of absorbing *all* the evolved H_2S .

It is sufficiently rapid to suit the most fastidious, as it requires no more time than is required to make the sulphur determination in the ordinary routine of laboratory work.

Below I add a few comparative results obtained in the course of work about a busy steel plant laboratory, and which are not picked, nor were they made for the purpose of establishing the method of standardizing, as that had been in use almost four years before these results were obtained, but were made for the purpose of convincing the president of a certain furnace company that our method of sulphur determination was accurate and comparable with that used by his chemist.

The determinations by the iodine method were made by my assistants, those by Br and HCl by myself.

Car 2238.	By Iodine, .067% S.	By Br and HCl, .063% S.
" 2238. 2d sample.	" .060 "	" " .064 "
" 3614.	" .069 "	" " { .072 "
		" " { .071 "
" 4326.	" .080 "	" " .075 "
" 4326. 2d sample.	" .069 "	" " { .064 "
		" " { .063 "
" 8113.	" .073 "	" " { .068 "
		" " { .068 "

The above are all the comparative determinations made at that time, October and November, 1890.

ON THE DETERMINATION OF SOLIDS IN WATER.*

BY ALLEN HAZEN.

A large number of experiments have been made during the last three years at the Lawrence Experiment Station with the use of sodium carbonate in making solid determinations, in the endeavor to make the loss on ignition show with some degree of accuracy the total amount of organic matter present in waters. While the attempts have not been entirely without success, the reduction of nitrate by the organic matter present, and the decomposition of magnesium carbonate, even at comparatively low temperatures, increased the loss, in the case of ground water and effluents, to a considerable extent. In surface waters with comparatively little

*From advance sheets of The Technology Quarterly sent by the Author.

mineral matter in solution, the sources of error from the above mentioned causes are very slight.*

The easier and more accurate determination of albuminoid ammonia and oxygen consumed from permanganate answered our purpose so much better that the determination of loss on ignition was finally abandoned.

It was shown by our experiments that the total solids obtained with the use of sodium carbonate, after deducting the weight of the soda used, is an accurate measure of the solid matter present—far more reliable than the simple residue of evaporation without soda.

If a solution of magnesium chloride is evaporated without soda, as in the usual course of water analysis, there is more or less hydrochloric acid lost, and the residue contains a large and variable amount of water of crystallization; so that the weight of the residue depends very largely upon the manipulation, and it would probably be impossible to proceed in such a way as to make the result correspond accurately with the amount of salt taken in every case. If, however, an excess of sodium carbonate is added before evaporation, the magnesia is precipitated as carbonate, while the chlorine remains in solution as sodium chloride with the excess of soda. On evaporation to dryness there is not a trace of hydrochloric acid lost, and the residue contains no water of crystallization and is not deliquescent. Its weight is practically constant under widely differing conditions of manipulation, and, after deducting the weight of the soda used, represents accurately the weight of the anhydrous magnesium chloride originally present; for, in the double decomposition there is no change of weight.

The same can be said of all magnesium salts, and with calcium salts the results are even more exact, owing to the greater stability of calcium carbonate and the ease with which it is dried at 100°.

That this is practically the case is shown by the following table of results with solutions of various salts evaporated to dryness at 110°, and, after weighing, igniting in a radiator.

*See paper on the Loss on Ignition in Water Analysis, by T. M. Drown, *Technology Quarterly*, December, 1888; *Chem. News* v. 59, p. 272. This Journal 3, 142.

Table Showing the Residue of Evaporation of Solutions of Various Salts, with and without Sodium Carbonate.

Salts Taken.	Amount Taken Grams.	Total Solids.	Loss on Ignition.	Fixed Residue.
Distilled water	100	.0001	.0000	.0001
Distilled water with sodium carbonate, after deducting the amount added	100	.0004	.0000	.0004
Sodium carbonate0133	.0135	.0002	.0133
Sodium carbonate0265	.0270	.0000	.0270
Sodium chloride0250	.0248	.0000	.0248
Sodium nitrate0212	.0220	.0001	.0219
Sodium nitrate with sodium carbonate0212	.0217	.0001	.0216
Potassium sulphate0100	.0102	.0000	.0102
Potassium sulphate0250	.0250	.0000	.0250
Potassium sulphate with sodium carbonate0100	.0118	.0010	.0108
Potassium sulphate with sodium carbonate0250	.0266	.0006	.0260
Potassium nitrate0072	.0076	.0000	.0076
Potassium nitrate0200	.0204	.0003	.0201
Potassium nitrate0200	.0200	.0002	.0198
Potassium nitrate with sodium carbonate0072	.0071	.0003	.0068
Potassium nitrate with sodium carbonate0200	.0214	.0009	.0205
Potassium nitrate with sodium carbonate0200	.0209	.0005	.0204
Calcium chloride0101	.0134		.0146
Calcium chloride with sodium carbonate0101	.0103	.0000	.0103
Calcium chloride with sodium carbonate0338	.0347	.0003	.0344
Calcium chloride with sodium carbonate0338	.0340	.0003	.0337
Calcium carbonate dissolved in CO ₂ water0480	.0492	.0003	.0489
Magnesium chloride0200	.0390	.0290	.0100
Magnesium chloride0200	.0362	.0262	.0100
Magnesium chloride0400	.0742	.0540	.0202
Magnesium chloride with sodium carbonate,0200	.0211	.0058	.0153
Magnesium chloride with sodium carbonate,0200	.0209	.0036	.0173
Magnesium chloride with sodium carbonate,0400	.0392	.0066	.0326
Magnesium chloride with sodium carbonate,0400	.0435	.0053	.0382
Magnesium carbonate in CO ₂ water0113	.0136	.0052	.0084
Magnesium carbonate in CO ₂ water0188	.0219	.0058	.0161
Magnesium carbonate in CO ₂ water0376	.0427	.0156	.0271
Magnesium carbonate with sodium carbonate0188	.0220	.0059	.0161
Sugar0050	.0065	.0050	.0015
Sugar with sodium carbonate0050	.0067	.0049	.0018
Sugar with .0212 gr. sodium nitrate0050	.0267	.0070	.0197
Sugar with .0212 gr. nitrate, and sodium carbonate0050	.0286	.0092	.0196

A sample of water, rich in salts, but with little organic matter, gave the following results :

	Without Soda.	With Soda.
Total solids	30.5	25.1
Loss on ignition	8.3	0.7
Fixed residue	22.2	24.4

Without soda the total solids are too high, on account of water of crystallization, and the fixed residue is too low, because a large part of the chlorine and nitric acid combined with the magnesia were lost on ignition. With soda, the total solids may be taken as an accurate measure of the solid matters present.

LAWRENCE EXPERIMENT STATION,
MASSACHUSETTS STATE BOARD OF HEALTH.

THE MANUFACTURE OF PHOSPHORUS.

BY EDWARD HART.

This substance was first prepared by Brand, of Hamburg, by evaporating urine and distilling the residue, and this process was the one universally described in the text books for a long time afterwards. The writer remembers to have read in a book upon chemistry by Naumann directions somewhat as follows for preparing it: Take 80 gallons of urine, evaporate it to dryness, and distill the residue in a retort, and you will obtain—an ounce of phosphorus. In many cases the yield seems not to have been so large, for in 1737 Hellot obtained the same amount of phosphorus from 700 liters, or about 175 gallons of stale urine.* It is curious to learn that it was known at this time that the urine of beer drinkers contained more phosphorus† arising from the phosphates from the grain used in beer brewing. Scheele dissolved bone ash in nitric acid, precipitated the lime with sulphuric acid, evaporated the filtrate to a sirup, mixed it with charcoal, and distilled it. Scheele also obtained phosphorus by another method from cold-short iron. The iron was dissolved in dilute sulphuric acid, and the solution diluted with water and allowed to stand until about a drachm of precipitate had deposited. This was washed and boiled with caustic lye, the lye was filtered off and neutralized

*Neues Handwörterbuch der Chemie 5, 318.

†Graham Otto, 2, 274.

with nitric acid, which caused the separation of a brown precipitate. This was filtered off and the solution mixed with mercurous nitrate. The precipitate mixed with fine charcoal was distilled in a glass retort, when mercury and then phosphorus distilled over into the water into which the retort neck dipped. Scheele used the same method for obtaining phosphorus from other phosphates.* Scheele's first method was then simplified by Nicholas and Pelletier† and Fourcroy and Vaquelin‡ who treated burned bones directly with sulphuric acid. From that time until the present phosphorus has been made by this process, and the text books repeat the same description as to the conversion of the bone ash into superphosphate, the passage of this by heating into metaphosphate, and the final decomposition by charcoal at a high temperature into phosphorus and bone earth.

A somewhat novel form of this method has recently been described by J. B. Readman.§ According to Readman, phosphoric acid is first prepared by grinding one of the calcium phosphates to a fine powder [according to Graham Otto the powder must not be fine, otherwise it forms lumps when treated with acid], and treated with chamber acid of 1.45 sp. gr. in wooden tuns made of pitch pine or other suitable wood, and provided with agitators also made of wood. Open steam is blown in during the operation, and sufficient acid is added to convert all the lime present into sulphate. After several hours' agitation, the contents of the tuns are run off upon large wooden filters lined with lead having false bottoms, or having ashes in layers of various sizes spread over the floor of the filters. [Wooden filter presses would certainly allow of much more perfect extraction and with less wash water.] The phosphoric acid passes through these filters as a bright, clear sherry-colored liquid having at first a sp. gr. of 1.17, which becomes reduced as washing goes on to 1.01. Special precautions are observed to avoid cracks on the surface of the gypsum contained in the filter, the formation of which would afford too ready an outlet for the wash water. The phosphatic gypsum left behind on the filters contains 71.14 CaSO_4 , 6.56 $\text{Ca}_3(\text{PO}_4)_2$, 12.10

*Hermstadt's translation of Scheele's works 2, 387.

†Journ. Phys. 11 and 28.

‡J. Pharm. 1, No. 9.

§J. Soc. Chem. Ind., Feb., 1890.

"silicious matter," 5.55 oxide of iron, alumina and organic matter, and 4.65* combined water and moisture. [It is evident from these figures that considerable free sulphuric acid must be contained in the solution.] The liquor is blown by one of the acid-resisting steam elevators or "blow jacks" to stock-tanks, and from there it is run by gravitation to the evaporators, which are circular tanks made of iron or wood, lined with thick lead, and heated by means of high pressure leaden steam coils. Each evaporator is provided with an agitator, which is kept in motion during the evaporation. Sulphate of lime is deposited as the evaporation advances, and so great does this deposit become that filtration or decantation is necessary before the acid attains the degree of concentration required. If no agitation is employed during the concentration, the gypsum attaches itself firmly to the coils, forming around them a thick coating, which must be removed by chipping. When the solution reaches sp. gr. 1.4 or 1.5, the evaporation is stopped and the gypsum separated. The solution now contains about 60 per cent. P_2O_5 , and should be free from lime. The strong syrupy acid is now mixed with 25 per cent. of coarsely powdered coke or charcoal, and carefully dried, either in iron pots or a muffle furnace, so as to expel all the moisture, sulphurous acid and hydrocarbons, and stored in air-tight iron boxes to await the distillation.

The distillation is carried out in small-bottle shaped retorts made of the best weathered and prepared Stourbridge fire-clay; these retorts or pipes are about 3 feet long by 11 inches external diameter, the clay being about 1 inch thick. The retorts are placed in a furnace something like a Belgian zinc furnace in construction, but having only two tiers of retorts, each row being placed back to back with their narrow mouths projecting an inch or so through the brickwork. There are 28 retorts in one furnace, that is to say, there are seven retorts in the first tier and seven directly above them on each side of the furnace. The mouths of the retorts are connected with the condensers by 2-inch malleable iron or copper pipes, which are luted to retort and condenser with clay joints. Hot water is used in the condensing trough, so that when the phosphorus is condensed it fuses and runs down by

*If these figures are correct, it is evident that a large part of the calcium sulphate is present as anhydrite, as 71.14 $CaSO_4$ requires almost 19 of water to form gypsum.

gravitation to the lower end, and may then be conveniently lifted out with a ladle.

Each retort holds between 20 and 30 pounds of the phosphorus mixture, and yields up the phosphorus existing in the free and uncombined phosphoric acid in about 15 hours. The 2-inch pipes are then disconnected, the residue rapidly withdrawn, and the retorts refilled, the heat being steadily maintained. Should a retort be cracked or fused either during the distillation or at charging, any phosphorus mixture it may contain is withdrawn, the dampers are closed, and the retort withdrawn from the furnace; a new retort, heated in an adjoining kiln to the required temperature, is substituted, and all proceeds as before. The crude phosphorus thus obtained has a dark mahogany color. It is fused under water in a lead-lined steam-jacketed kettle and about 4 per cent. potassium bichromate added. The mixture is stirred for half an hour by means of the agitator, the same weight of oil of vitriol is then added while the stirring is going on. The impurities are in this way oxidized, leaving the phosphorus pure and nearly colorless. Another method is to refine by distillation in an iron retort, and Readman thinks a combination of both methods is "in some way desirable." The phosphorus is then molded into sticks or wedges. The wedges are made by melting the phosphorus and transferring it into circular tin dishes 10 inches in diameter by 4 inches deep, and when filled a star-shaped mould is introduced into each, which divides the circle into 10 wedge-shaped pieces suitable for packing into tin cases. After this cold water is introduced, which soon solidifies the phosphorus and admits of its easy removal.

This process, which is essentially the method described in the text books, with modifications, is a very wasteful and unsatisfactory one; about 17 per cent. of phosphorus is contained in bone, ash of which about 11 per cent. should be recovered by distillation if the reactions given in the text books are correct. In practice only 4.4 to 10 per cent. is obtained [according to Payen, 8-10, according to Fleck, 100 parts fresh bones give 4.4 parts phosphorus and Violet obtained 5.7 parts]. The loss is caused partly by the formation of phosphoretted hydrogen which escapes, and partly by the escape of phosphorus vapor from cracks and pin holes in

the retorts. The price of phosphorus is now about 60 cents per pound, and when it is considered that the price of phosphorus in phosphate of lime is approximately rather more than 3 cents per pound, we can begin to appreciate the defects of the process. Only a part of this defect is due to the difficulties of drying and distilling. A still larger share is due to the large plant required, the large amount of labor needed and the large number of operations, each of which involves considerable waste. A better method is therefore greatly needed.

Wöhler's suggestion that sand be mixed with the phosphate and the mixture distilled in clay retorts seems never to have been successfully carried out. According to most writers on the subject the chief difficulty in the way has been the high temperature required, which is destructive to the retorts and causes a large consumption of fuel.

By using this mixture of sand and calcium phosphate, and heating at a very high temperature with a fire urged by a blast, Readman* succeeded in getting 72.2 per cent. of the phosphorus contained in the mixture in the form of crude phosphorus. Of a total amount of 2732 grains phosphorus in the mixture used, 295.8 grains were left in the slag, 74.2 grains were left in the retort in the form of phosphide of iron, 1730 grains were condensed, and 273 grains escaped condensation. The same reaction takes place at a much lower temperature when china clay is used instead of sand. It became evident that retorts were not suitable for this process, since they are of small capacity and will not long resist the high temperature and the corrosive action of the slag. Readman,† therefore, endeavored to effect the decomposition by charging the materials with coke into a cupola furnace. This style of furnace was, however, found unsuitable for the purpose. "The large volume of air required, and the difficulty, or perhaps impossibility, of driving off the phosphorus by the time the phosphorus-bearing material passed the tuyeres of the furnace, were serious obstacles to success. All the air that was passed into the furnace produced gases which had to be cooled and dealt with when they left, for they contained all the phosphorus that was expelled from the material. Then again, the slag passing the hottest part of

*J. Soc. Chem. Ind., May, 1890.

†J. Soc. Chem. Ind. X, 445.

the furnace and yet retaining much material only partially decomposed rendered the former highly infusible and difficult to tap, and sooner or later caused 'scaffolding' and choking of the furnace."

In conjunction with the Cowles Co. of Milton, Readman finally applied the electric furnace to the reduction of phosphorus, using as a charge the mixture of phosphate, sand and carbon, after encountering and surmounting various difficulties, with entire success.

New experimental works for this reduction process have been erected by Readman, Parker and Robinson (Parker and Robinson had been working on the same lines) at Wolverhampton.

"The process is carried out in the following way: The raw materials all carefully and intimately mixed together are introduced into the furnace. The current is then turned on and shortly after indications of phosphorus make their appearance; the gases from the furnace pass away to large copper condensers—the first of which contains" hot and the others cold water—and finally they pass on to the air. As the phosphorus is distilled off from the mixture, the residue in the furnace forms a liquid slag, which from time to time is tapped out at the bottom of the furnace, fresh phosphorus-yielding material being introduced at the top. In this way the operation is a continuous one, and we have every reason to believe it can be continued for days without intermission." The electric furnace used is similar in construction to the Cowles furnace, but in order to avoid concentration of heat, small furnaces are used capable of yielding about one-and-a-half hundredweight per day. About 86 per cent. of the phosphorus contained in the charge is obtained, provided the charge is free from iron, and almost any phosphatic material may be used if it contains no iron. When iron is present, phosphide of iron is formed and a greater loss of phosphorus sustained.

In the United States the chief, perhaps the only, manufacture of phosphorus is the firm of J. J. Allen's Sons, of Philadelphia, who have a plant at Mount Holly, N. J. They have a contract with the Diamond Match Co., the chief consumer of phosphorus. The manufacture is carried on by the old process, but for some time past this firm has been actively seeking for a better method.

THE PURIFICATION OF WATER BY METALLIC IRON.*

BY HENRY LEFFMAN, M. D.

My purpose in the present contribution is to briefly explain and demonstrate the efficiency of a simple process of purifying water. Of the value of such process it is not necessary to speak. Not only do the requirements of sanitation demand pure water, but many manufacturing industries cannot be carried on without such supply. It will not be necessary for me to detain you with the history of the process, except to say that it originated in an effort to improve the water supply of the city of Antwerp, about six years ago, at which point the only supply available to the company which had secured the franchise was a river very turbid and impure. The success of the system on a large scale for the past six years at Antwerp, and for shorter periods, at other places, has been attested by the reports of experts and the statements of impartial observers, among the latter being a member of the State Board of Health of Pennsylvania and a member of the Board of Trade of this city. The practical process may be explained as follows :

Metallic iron in the form of either cast iron borings or steel punchings is placed in a cylinder so arranged that, by a slow rotation, the iron may be continuously showered through the water, which is being passed at moderate speed through the same cylinder. The cylinder is provided with pipes, by which air may be introduced in direct contact with the iron, if necessary. The chemical action consists in great part in the conversion of the iron into ferrous carbonate (protocarbonate of iron) through the agency of the carbonic acid, which partly dissolves in the water and partly remains suspended in the form of dark green turbidity. On exposure to the air the iron is converted into ferric hydroxide (hydrated sesquioxide of iron) which, settling rapidly, carries down with it and oxidizes the organic matter. The flocculent sediment permits of rapid and perfect filtration through a simple sand filter.

The process may be carried out in the laboratory in such a manner as to exhibit results as they would be obtained in the

*A Paper read at the Eleventh Annual Meeting of the American Water Works Association.

actual treatment. It has thus been possible to examine the behavior of waters of different types, and to determine the most satisfactory system of application.

A process of this kind, essentially simple, does not require for its correct presentation an elaborate discussion of the theories of the action. For evidence of its efficiency, I think I can best point to the continued successful application of it to the purification of the waters of Antwerp, Dordrecht, Paris, Nancy, and other places.

The advantages of the Anderson process, as this method is called, over other methods of purification and filtration, are among others :

1. The avoidance of the use of chemicals.

Far from exciting prejudice, the idea of putting rusting iron in contact with drinking water, is one that has been familiar to the public mind from time immemorial. Scientifically utilized, as in the Anderson process, metallic iron, by its mere contact with impure water, produces by the help of the ingredients of the waters the salt necessary to produce purification. Natural oxidation causes this salt to act as a coagulant, and further, the action of the ferric oxide, or rust in its nascent state, furnishes the power of destroying organic matter by a process which has been likened to the burning of holes in linen by rust stains or iron mould.

2. The automatic and continuous renewal of the active surface of the iron.

By means of the Revolving Purifier system (the technical name for the process), the various forms of iron previously recognized as efficient purifiers of water can be utilized, without incurring the mechanical difficulties resulting from their use in filters which become choked up and caked after a short time.

The iron being in a constant state of agitation, no choking nor caking together of the purifying medium is possible. The particles of the finely divided metal are kept rubbing against one another, and new surfaces are brought into contact with the water, which in its flow carries out of the cylinder the iron which has been dissolved by chemical action with the impurities contained in the water. Owing to the completeness of the contact between the iron and the water and the large surface of metal exposed,

purification is effected in $3\frac{1}{2}$ to 5 minutes for moderately bad water, and in 5 to 16 minutes for sewage effluents.

Again, it is evident that any purifying material spread out in a filter is constantly reducing the area of its active surface, by the formation of the compounds which it makes in removing the dissolved impurities of the liquid it is filtering. The degree of purification effected must, therefore, constantly decrease until steps are taken to remove the products of the purifying action, and to revivify the purifying material. This has always been one of the greatest difficulties encountered when endeavoring to purify water or sewage, on any scale of greater magnitude than that of a laboratory experiment, or of a domestic filter. The Revolving Purifier entirely overcomes this difficulty by the constant rubbing together of the particles of the purifying material, and the carrying away by the liquid itself of what we may generally term the products of the purification.

3. The removal of micro-organisms to such an extent that the water as delivered is practically sterile.

This extraordinary fact is conclusively proved by the experiments made at Antwerp, by Professor Van Ermengem, on samples drawn at frequent intervals from the delivery pipes of the sand filters when supplying over two million gallons per day. The one hundred thousand microbe colonies contained in a cubic centimeter of the Nethe water are reduced to an average of five colonies, which, considering the great difficulty of avoiding all contact with the air in these delicate tests, is equivalent to a complete destruction of the micro-organisms.

The observations show that the process is applicable to the purification of all classes of natural waters. Waters turbid from suspended clay or sand, or colored by vegetable matters, are especially susceptible of rapid and complete clarification by it. In all cases, chemical tests of the treated water show marked diminution in the organic matter, and the filtered water is practically sterile.

Among the numerous results, I record the following as exhibiting the effect of the process on waters of different and familiar types. For estimating the reduction of the organic matter, the acid-permanganate method was used, since, although not wholly

trustworthy for determining the sanitary value of a given sample, it is convenient, and suffices for comparison between various samples of the same water. The figures are in parts per million.

A sample from Wilmington, N. C., strongly colored by dissolved organic matter, but not turbid, was treated, and the oxidizable matter determined. The results were as follows :

	Before Treatment.	After Treatment.
Oxygen absorbed at 212° F.	14.20	2.44

The filtrate was clear and colorless.

The efficiency of the process in its application to turbid river waters is well shown in an experiment on the Mississippi water. This contained much suspended matter, which after many days' standing did not perfectly settle, and could not be filtered clear. Treatment in the laboratory by the iron process gave results that were most satisfactory. After shaking with the iron, and aerating by standing for a few minutes in an open vessel, the ferric hydroxide separated in large flakes, which permitted of prompt and rapid filtration, yielding a perfectly clear filtrate. To determine the degree of chemical purification, the oxidizable organic matter was determined as follows :

	Before Treatment.	After Treatment.
Oxygen absorbed at 212° F.	2.88	0.36

715 WALNUT ST., PHILADELPHIA.
July, 1891.

SAMPLING ORES WITHOUT USE OF MACHINERY.*

BY WILLIAM GLENN, BALTIMORE, MD.

The taking of proper samples of crude ores seems to be less thoroughly understood, or less carefully practiced, than its importance requires. We all know how often we encounter the reports of very accurate assays and analyses, the weight of which as evidence wholly depends on the method of obtaining the sample, and is very probably *nil*, because there has been no proper sampling. Passages might be cited from technical books, and from current technical literature (all the work of writers whom we

*From Transactions of the American Institute of Mining Engineers. Cleveland Meeting, June, 1891.

delight to honor) to show that even among high scientific authorities there is too little acquaintance with the practical art of the sampler. There is no metallurgical or chemical establishment which does not frequently receive samples truly representing nothing. They consist usually of bits of ore, or what not, selected because they are worse or better than the average of what they are meant to represent. And they are worthless, no matter who made the selection. Where conscious choice is permitted to enter into the operation, a fair sample will not result, unless by a miracle.

The work of sampling is often looked upon as within the realm of boys and pensioners only. At least, though the manual labor be left to subordinates, the principles on which it is conducted and the safeguards with which it is surrounded are not unworthy of the study of experts; and experts should be ready to teach these principles and enforce them in practice. For exact sampling is the indispensable first step towards learning the value of any boxful, carload or shipload of ore.

I propose to give a simple account of the method of sampling by hand, such as I have always pursued. There is nothing new about it. So far as I know, it is the immemorial old method, as old at least as Cornish copper-mining. Perhaps my fellow-members in the Institute may suggest improvements in it. If not, it will constitute a record in our *Transactions* to which laymen and beginners may be referred.

There are two principal processes to be considered: first, how to take the gross sample of the lot of ore; second, how to proceed with that sample. Really, there is no iron-bound rule governing the first step; each may have a way of his own; yet most samplers proceed in much the same way. But once having the rough sample, there is no question as to what shall be done with it. It is to be worked down after the orthodox fashion. It must be broken and mixed and quartered until only a few ounces remain. The sampler bottles this residue; the chemist does the rest.

Assume that we have a rough sample, weighing a ton, of any ore with its gangue. Assume that by some manner of magic we can at once reduce the whole of it to dust. Evidently, if we could mix it long enough and well enough upon a clean, tight floor, it would finally become homogeneous. In that case, we could fill

half a dozen small bottles from any part of the pile, and they would be fair samples. But the work would have to be admirably done; so well done that a single gramme taken from the pile would properly represent the entire ton of sample. Really, this would entail a great deal of labor. And if the rough sample weighed 15 tons or more, as it would if taken from a shipload, the bare labor of mixing that quantity of dust until homogeneous is wearying even to think of. We cannot proceed upon the proposition that a final sample may be obtained in any such way. Yet upon a rock similar to this many are wrecked.

To take, for illustration, a definite case, let us assume that we have to sample a 10-ton pile of 10 per cent. copper-ore, prepared for market. It will consist of masses generally the size of one's fist, but of all smaller masses and even of dust. We shall require for the work a clean, tight floor or pavement, an iron mortar and pestle, a shovel, a small hammer, a piece of iron for an anvil and, lastly, a broom. Besides these, we shall find convenient a wheelbarrow or a barrel or box of some kind.

For convenience and force I will put my description into the form of homely directions, such as I might give to my workman.

Begin by shovelling the pile roughly into the form of a flattened cone or a flattened pyramid; say we choose the pyramid. Now make a trench straight through the pile, cutting it into two nearly equal parts. And again by a trench (at right angles to the first) divide these halves into four nearly equal quarters. A part of the ore taken from these trenches will form the sample required. Proceed as follows:

Having the wheelbarrow ready, begin at the middle of any side of the made-up pile and cut the first trench. Cast the first shovelful to the right, the second to the left, the third into the wheelbarrow. Repeat this order of shovelling until the barrow is full, then empty it upon the well-swept floor intended to receive the sample. Continue in the same way until the trench has passed through the pile, when there will result two rather long and narrow piles. Begin the second trench, extending it across the middle of the two piles, casting the first shovelful right, the second left, the third in the barrow. Proceed in the same as with the first trench. When done, you will have shoveled about 6000 pounds of ore. As every

third shovelful was thrown into the barrow, there will result about 2000 pounds of sample upon the floor. That this is a fair sample of the original pile is based upon the assumption that each third shovelful thrown into the barrow was like the first and second ones cast into the piles. The hypothesis is reasonable and freely to be trusted.

Having the sample, proceed with it after the regulation method, as follows:

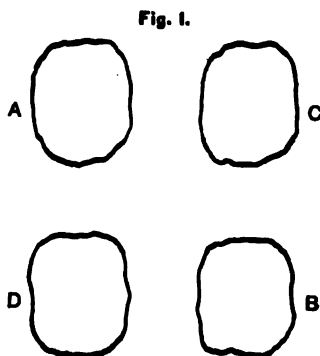
Spread it thinly upon the floor; now examine it. If there be any lumps which look larger than the general run, place the anvil upon the pile, and between that and the hammer break those lumps. The next step is to thoroughly well mix the sample. Begin at one edge of it and shovel the ore over upon itself. Move around to the opposite side of the pile, and from that side shovel the ore again upon itself and back to its original place upon the floor. Having it well mixed, form it into a flattened cone and sweep all the dust upon and around the pile. You have now to halve and quarter the sample as follows:

Commence at any point and shovel a road through the centre of the pile, casting the shovelfuls alternately right and left as you proceed. This movement will result in cutting the pile into two elongated nearly equal ones. Beginning at the middle of one of them, shovel a road through it in the same way as was done before. And in precisely the same way cut the other pile in two; sweep upon each pile the dust belonging to it. These movements will result in four piles, as in Fig. 1.

If the sample were well mixed, when and as directed in these notes, then will each of the quarters, A, B, C, D, have the same composition as have all the others. But if upon inspecting them, you judge one or another to be poorer or richer than the others, you will have then sufficient evidence that the work has been badly performed. In that condition of affairs, mix well together all the piles, and once more halve and quarter them. Having made all the quarters of the same composition, it follows that any two of them may safely be accepted as representing the original 2000 pounds of rough sample. This opens a road leading in the right direction, since it enables us finally to get rid of half the sample. We may cast out two of the quarters and retain the other two for

the sample. It is a matter of indifference which two are retained, say A and B. Remove from the floor C and D, together with the dust belonging to them.

We have again to break the larger stones, until there remain none larger than walnuts. Place the anvil between the piles, within easy reach of them. Take a stone from A, break it; take



PLAN OF ORE-PILES AFTER QUARTERING.

one from B, break that. Continue in this way, taking stones alternately from each pile, until all are reduced to the size stated. By proceeding in this way, the sample is more or less mixed while being broken. Complete the mixing as before, by shovelling all of the sample forth and back over the floor. Form it once more into a flattened cone, and sweep the dust upon and around it. Divide the cone into two halves, and those into four quarters, precisely as you before did, and as illustrated in Fig. 1. You have now to reject two of these quarters. The unwritten law of the sampler says that it must be those holding the positions A and B, because those were retained in the last quartering. Remove A and B from the floor, retaining C and D for the sample. These would now weigh about 500 pounds.

Proceeding as before, break down the lumps of ore until none are left larger than say 1-inch cubes. Again mix well the sample, make it into a pile, sweep up the dust, halve and quarter the pile. Reject two quarters (C and D, of course), retain two, precisely as in former quarterings.

Once more break the lumps, this time down to half-inch cubes.

Mix well the sample, make it into a pile, sweep up-the dust, halve and quarter, reject two quarters. The two quarters retained would weigh about 125 pounds. Break it down until comparable to fine gravel and coarse sand. Mix and quarter once more.

The two quarters this time retained would weigh about 60 pounds. With the mortar and pestle break this to something approaching coarse sand. Again mix and quarter. The quarters this time retained are to be ground yet finer, mixed and quartered.

If you have no mortar and pestle, the hammer and anvil may be substituted throughout. After getting the material into the form of coarse sand, it is best to mix and quarter it upon a sheet of paper, even an old newspaper.

At this point the sample would weight about 15 pounds ; its larger grains would be in size like coarse sand. It would be safe now, without further breaking, to mix and quarter it twice, or until its weight did not exceed 4 pounds. Run this through the mortar and then mix and quarter it twice, or down to 1 pound weight. Grind this to something approaching powder, and, for the last time, mix and quarter it. Have ready six wide-mouth one-ounce bottles. Place them in a line, side by side, upon a sheet of paper. From the other paper pour the ground sample in a small stream, forth and back across the mouths of the bottles, until they are all full up to their shoulders. Cork, seal and lable them, and the sampling is done, and properly done.

If there should lurk in your mind a suspicion that this half-pound residue of dust may not, after all, properly represent the rough sample with which you began, go back over the work, and try to decide precisely where in the quarterings the sample retained ceased to be a sample. If you can decide upon that point exactly, then you will know just where you failed to do your work properly. The error will be with you and not in the method.

It does not, in the slightest, matter of what solid a sample may consist, or how much or how little it may be, it should be worked down in the manner just detailed. Whether a sample consist of 20 tons or 1 ounce, it matters not, except as to breaking and grinding.

A word may be added as to larger and rougher ore-piles than have as yet been mentioned. It is not unusual for one to have a

pile of 100 tons, or 200 tons, which one would like to sample. Such piles are apt to consist of lumps larger than a man's head, together with masses of all smaller sizes. Where a pile is formed by dumping ore uniformly upon its top, the likelihood is that the pile is homogeneous. In such a case, it is safe to make short cuts into it at several points around its base, and to consider as sample the ore so gotten. It is safer to make one cut through the pile, retaining as sample each third shovelful, as in the case of copper-ore we have just considered. In forming ore-piles of the weights given, it is a good custom to put upon a separate platform each tenth or twentieth barrow-load coming from the mine; the small pile will prove a fairly good sample of the large one. But no matter how it may be gotten, the rough sample is to be broken and mixed and proceeded with after the regulation method.

No account is here taken of moisture-samples, or of sampling train-loads or ship-loads. This paper is meant to help beginners, but it would be, in the writer's judgment, a benefit to others also, if our members who are practically acquainted with sampling would present their own methods with regard to the various branches of the art. The precautions specially required in sampling rich silver-ores, for instance, might well be made the subject of comparison and discussion.

DISCUSSION.

R. W. Raymond, New York City: I am glad that this subject has been brought to the attention of the Institute. Mr. Glenn has by no means over-stated its importance: and yet, with the exception of the paper of Mr. D. W. Brunton (*Trans.*, xiii., 639) describing a mechanical ore-sampler, I can recall little or nothing in our *Transactions* concerning it. The practice in the West, with regard to silver-ores, etc., is affected by various considerations. As a general rule, such ores are either already fine or are crushed before treatment. I think it is now generally admitted that a good mechanical sampler connected with the crushing-machinery takes a fairer average sample (usually one-fifth or one-tenth of the total lot of ore, according to the richness and the consequent importance of exact determination of value as a basis of payment to the miner) than can be got by throwing aside the fifth or tenth

shovelful in unloading. At all events, the mechanical sampler cannot be suspected of bias, conscious or unconscious; provided it is so constructed as to deliver impartially the coarser and finer particles of the stream of ore passing through it. Disputes are therefore avoided by using it.

But for many classes of ore, the sample is still taken with the shovel; and it is after this has been done, whether mechanically or by hand, that the process begins, which can properly be compared with that described by Mr. Glenn. The differences between this process and his are required by the following principal considerations:

1. The material, namely, ores carrying, besides, lead or copper, more or less silver and gold, is so much more valuable that small errors in determinating its contents may be the source of the large loss to the buyer or seller.

2. It is almost always finer than the crude material contemplated by Mr. Glenn. Either it has been crushed before the sampling begins or it is so generally fine when received that the preliminary stages of sampling may be, in the judgment of the manager, performed without crushing. This, however, always involves a risk, the assumption of which by a prudent manager is justified only when the conditions are favorable; for instance, when the character of the ore is well-known; when its grade is not too high; when the difference in richness between coarser and finer pieces is not so great; when careful experiment has shown that sampling without a preliminary crushing is sufficiently accurate; when avoiding the extra cost of crushing would be an important saving, or when the crushing machinery of the establishment is fully occupied with material which must be reduced before sampling. The nature of the contract between the smelter and the miner is another element to be taken into account. Perhaps the ore is not to be paid for strictly according to sample-assay (a thing which now and then happens, though not often, in the purchase of large dumps at a round price, or the treatment of ores on joint account, to be settled by the net results, instead of the preliminary assays, or under special contracts, in which the loan of money or other inducement to the miner has secured special terms). Perhaps, again, the smelter owns the mine, and can thus afford to save cur-

rent expense by taking some risks in sampling his own ore which he would not take with ore for which he had to pay according to the sample-assay.

I think it may be said, however, that the sampling-works proper, that is, those which are not parts of smelting-works, but stand between the smelter and the miner, as agents for the latter in the sale of ore, warranting to the purchaser the accuracy of their determination of its contents, always crush everything they receive. And I think it may be said, also, that when the capacity of crushing and sampling-apparatus is adequate, and the arrangements for receiving and handling ore so perfect as to avoid both demurrage on railway-cars and re-handling of material, the crushing and mechanical sampling of all lots received is not only better, but cheaper, than shovel-sampling of crude cargoes. The matter may indeed be left to the discretion of a competent manager; but the most competent managers are not anxious to multiply the matters which are left even to their own discretion, still less to the discretion of subordinates. There are innumerable things which have to be watched daily and hourly around great smelting-works; and it is a relief when any one department can be placed in the category of comparative routine, calling for fidelity rather than discretion. Moreover, the exact determination of all the elements of an ore of the class here contemplated is as important on technical as on commercial grounds. Without it, the metallurgists can neither calculate his charges successfully nor be held responsible if he fails to do so. And the sample taken of each new lot of ore received is not only assayed for its valuable contents, such as lead, copper, silver and gold, and for sulphur, iron, silica and zinc (which may affect the price to be paid for it), but also analyzed for all its earthy bases, so that it may be properly mixed for smelting with other ores or fluxes. Now it is quite likely that the gangue-minerals of an ore may break very differently, according to their natural hardness or cleavage, in the ordinary processes of mining and shipment. Moreover, the same car-load from a given mine may contain ores from different slopes, varying so greatly in character and condition that even if the average of gold or silver were reasonably uniform, the average of silica, lime, magnesia, baryta, etc., would not be so, and the lumps

might be entirely different in these particulars from the finer stuff.

With these digressions and explanations, I repeat the general statement that the ore to be sampled in the West is generally fine. But for the rough sampling of ore at the mine, or in localities where proper crushing cannot be done, the procedure described by Mr. Glenn seems to be a good one for the preliminary stages.

3. Notwithstanding the general fineness of the crude pile, and no matter to what degree it may have been reduced by crushing (short of the final reduction to impalpable powder), there is still a distinction between coarser and finer particles, and in the majority of cases this distinction is one of value as well as size. Many of our western ores carry silver, for instance, not only as an accessory ingredient of galena, but also in the form of finely-disseminated "true silver ores" accompanying the galena. These are usually not only in fine crystals or specks to begin with (often not distinguishable to the naked eye), but brittle besides, so that the shocks and abrasion of mining, transportation, crushing and handling reduce them to still smaller size. In the stamp-mill they make "slimes." In concentration they are very likely to escape and leave the headings impoverished, though clean from gangue—"poor but honest," so to speak. In sampling, they present the greatest danger of error.

Something similar might be said concerning the tenor of gold in many ores. Although true gold-ores are not common, yet in a lot of ore consisting largely of auriferous pyrites, for instance, there will certainly be more or less oxidized material, in which there is fine, free gold. I confess, however, that so far as my observation goes, this is not the source of as serious difficulty in sampling as are the brittle ores of silver. That is a point on which I hope some of our members who have had wider practical experience with the sampling of gold-bearing ores will throw further light. My own knowledge comprises more particularly the practice of lead-smelters; and in that practice the gold in the ores purchased, though it is determined and paid for, has not been hitherto a point raising special questions of difficulty. Or rather, the precautions taken as to the fine dust of silver-ores cover the question of gold also, so that this has not called for separate con-

sideration. Moreover, almost all the distinctively gold-bearing ore of the country, as well as a great part of the silver-ore, is reduced by wet-crushing for amalgamation or other subsequent treatment, and consequently sampled by battery-assays—a process which is not here under consideration, and which does not encounter the precise difficulty just described. I am inclined to think that in lots of crude fine ore, or of ore dry-crushed for sampling, oxidized material containing gold would not present as much difficulty as silver-ore, because it is less likely to form fine flying or sifting or rolling dust. The iron oxide tends rather to pack or adhere—at least to lie where it falls—unless it has been artificially dried and pulverized.

But the difference of value between coarse and fine particles may be due to other minerals than those already mentioned. And there may even be cases in which the greater value is in the coarser material. I need not, however, enlarge further under this head.

4. Obviously such a difference would have no effect, if the whole mass to be sampled were so thoroughly mixed that the proportions of different sizes were uniform throughout. But this is not practicable, because the coarse and fine particles behave differently as to rolling and sifting over or through the pile upon which they are shoveled. Consequently, it becomes necessary, in order to secure a correct final average, to make the distribution of sizes in each pile formed *symmetrical*, since it cannot be made truly *uniform*. At a later stage, as will be seen, the whole of the sample thus secured is reduced to powder. Yet still the precaution of making symmetrical piles for quartering is continued to the last.

With these explanations I will describe the quartering of a sample of ore (say one-fifth or one-tenth of a gross lot) as practiced at some of the leading works in the West.

The mass is first shoveled into a ring on the sampling-floor, and this ring is then shoveled toward the center, each shovelful being carefully delivered upon the summit of the pile in the center, so that they shall roll equally in all directions. A conical heap having thus been formed, it is pulled down and spread out. The workmen walk round and round the pile, pulling with the shovel, as it were, the ore towards them, so that it rolls outward. The

lower six inches of the pile is not disturbed, and when this process is finished, the conical heap has become a truncated cone of larger base-area and six inches height. This flat heap is now quartered by pressing a stick or a board held edgewise down into it so as to mark the diametrical divisions. Two opposite quarters are cut out with the shovel and removed. The other two are again mixed, formed into a conical heap, and flattened out as before. This procedure is repeated until the quantity has been reduced to one or two wheelbarrow-loads, when, if the material has never been mechanically crushed, it is crushed in the rolls to say half-inch maximum size. The quartering is then continued till the sample has been reduced to a panful. This is ground say to 60-mesh size (after a partial preliminary drying, if necessary to facilitate the grinding in a rotary fine-crusher) and then taken to the assay-laboratory, where it is thoroughly dried (say for 24 hours at 212° F.), and rubbed fine until the whole will pass through an 80-mesh sieve. Quartering is then resumed and continued until the sample is only sufficient to fill three bottles, one of which is for the assay of the works, one for the customer, and the third for the umpire-assay, if such should be required.

The details of this practice may vary in different works, and I trust our members, many of whom are engaged in such work, will give us, in the way of criticism or suggestion, the benefit of their experience. It is perfectly evident, as Mr Glenn says, that a vast amount of skill and precision is daily wasted by our chemist in the delicate analysis of samples that mean nothing. To cite a single instance, I have recently studied with much interest the various papers in our *Transactions* concerning the practical results of the magnetic concentration of iron-ores. In Mr. Birkinbine's paper, presented at the New York meeting, there is a simple formula by which he calculates from the percentages of iron in the crude ore, the concentrates, and the tailings the quantity of crude ore required to furnish a ton of concentrates; and he applies this formula in testing the comparative economy of different magnetic concentrators. But in several instances the actual quantities of crude ore, concentrates, and tailings have been reported, and they do not agree with the results of calculation by this formula. Now the formula is mathematically accurate, and there is no reason to

doubt the accuracy of the chemical work. It follows that the samples, either of the crude ore or of the concentrates, or of the tailings, could not have been accurate. It is certainly to be desired that future tests of such work should include more thorough sampling, and that future accounts of such tests should include descriptions of the method of sampling employed. In the absence of certainty as to the fundamental data, the application of mathematics to the discussion of results seems to be labor thrown away.

INDUSTRIAL MANUFACTURE OF LACTIC ACID.

The production of lactic acid and lactate of lime by fermentation is described generally in chemical works, and has been the principal subject of a number of investigations, but the author agrees with M. Duclaux, when the latter states, in his report upon the advance of science in 1887 (*Encyclopedie chimique*, Frémy), that all the processes given are long and devoid of accuracy. The author points out a few of the errors and fallacies in these processes, and describes his own, which he claims differs from all preceding.

Preparation of the fermentable sweet wine.—For the successful evolution and multiplication of the lactic ferment, it is necessary to have within its reach, sugary nitrogenous and saline matters for aliment, and that the medium remain constantly neutral, and conveniently supplied with air. These aliments are furnished by the diastatic saccharification of malt, just as in brewing, except that the brew is kept longer at 50° C., in order to obtain more maltose and to reduce the quantity of dextrine to a minimum. The temperature is then raised successively to 60°, 63° and 65°, and finally brought to a boil to prevent an increase of nitrogenous matter, and to kill all malt ferments. This brew gives a sweet wine or liquor, containing albuminous or nitrogenous matters, and brine rich in phosphates. The wine, which is not cooled below 45° C., is put in a fermentation vat, and receives some carbonate to keep it neutral, and the lactic ferment.

Culture of the lactic ferment.—The lactic ferment is obtained by the processes of Pasteur or others, and it is built up and multiplied in Pasteur flasks, containing sterilized barley-wine, with the addition of pure and sterilized calcium carbonate, before being placed in the

fermentation vats. This ferment should be examined at each stage of its multiplication with the microscope, and should not be sowed in the wine until after its purity is assured. If only pure air is allowed to enter the vessel and consequently all germs avoided, its production in a state of purity presents no difficulty whatever.

Progress of the fermentation.—The fermentation may take place in a room heated to 45°, in which the vats are placed, but it is best to supply the heat to the vats by means of worms or thermisiphons, while the room is maintained at the ordinary temperature. Each vat is supplied with a thermometer, and covered with a water tight lid, through which pass two tubes, one bent in the form of a siphon to allow the disengaged carbonic acid to flow out, and the other to allow air to take its place the latter is loosely stuffed at the end with cotton, to prevent dust and impurities from entering. This tube approaches to the level of the liquid, and has its upper end supplied with a cock, by means of which the flow of carbonic acid through the gas siphon can be stopped at any time. The fermentation can be considered finished at the end of five or six days, if the proper temperature has been maintained.

Extraction of calcium lactate.—The extraction of calcium lactate is but slightly prevented by the presence of the albuminous matters which have not been consumed by the ferment. These nitrogenous matters are precipitated by a sufficient quantity of tannin, extract of oak, chestnut, or some other astringent tanniferous body.

Filtration gives a clear liquid, and from this, upon evaporation, lactate of lime crystallizes out.

The separation of lactic acid and the formation of other lactates from this is known.—*M. Georges Jacquemin (Bull. Soc. Chem., 5, 294).*

W. W. D.

NEW PROCESS FOR THE OXIDATION OF CHROMIUM ORES AND THE MANUFACTURE OF THE CHROMATES.

The ordinary method of manufacturing the bichromates consists in making an intimate mixture of, finely pulverized chrome ore, lime in large excess, potash or soda, or corresponding salts

of these two bases. This mixture is placed in a reverberatory furnace, and subjected to a high temperature, while plenty of air is supplied. During the operation the mass is constantly puddled to bring all the particles into contact with the hot air, so that all the sesquioxide of chromium of the ore will be oxidized. After the oxidation is finished, the mass is taken from the furnace, and cooled; the bichromate is obtained by lixiviation, treated with sulphuric acid and crystallized. This method of manufacture has several serious objections, to wit:

1. The enormous expense of the fuel used to obtain the high temperature in the furnace.
2. The costly and laborious manual labor.
3. Loss of alkalis, through volatilization, and carrying off with the hot gas; also by combination with the gangue, notably the silica, by forming silicates of potash or soda.
4. The impossibility of employing poor or silicious ores.
5. Loss of the ore not attacked, through imperfect puddling.

The processes that have arisen to obviate these defects may be classified under the four following principal heads.

1. Processes to reduce the cost of the manual labor.
2. Processes, by which instead of the combined carbonates of potash and soda, some less costly salts of the same metals can be used.
3. Processes, by which the temperature in the oxidation furnace is lowered.
4. Processes, by which part of the chromium oxide or the chromates lost in the operations can be recovered from the residues.

None of these processes materially effect any changes however, and the authors, after research and experiment have devised a solution to the problem, in a new process, following an idea suggested by Pelouze.

The ore very finely pulverized is mixed with chloride of calcium or lime, or carbonate of calcium, in such proportions that all the base, proceeding from the caustic lime or the carbonate of calcium put in the mixture, shall be in slightly greater quantity than is necessary to transform into chromate of calcium all the sesqui-

oxide of chromium of the ore, when this sesquioxide will be by oxidation changed into the chromic acid state. The chloride of calcium employed in the proportion of one equivalent for 3 of the total calcium, is most convenient for the formation of oxychloride of calcium. If the mixture is made with carbonate of lime (pulverized chalk), it will not stiffen in the air; but if lime and carbonate of calcium are employed at the same time, the mass stiffens like cement, and can be moulded into bricks or plates. The best way to operate, is to mix first a part of the ore and well pulverized chalk, and slake it with the necessary concentrated chloride of calcium solution; then to make up a lime dough, and mix the two, moulding quickly. The loaves or moulds thus formed, are partially dried in the air, then completely dried in a furnace at a moderate temperature, and finally baked, to effect the reduction of the carbonate of calcium into caustic lime. It is only necessary then to expose the loaves to the air at the ordinary temperature, for the oxidation of the sesquioxide of chromium will go on by degrees without any manipulation, by the action of the atmospheric air, the matter thus prepared having a sufficient porosity to allow the air free access to the interior of the mass. Under ordinary conditions the oxidation will be completed in a month. The division of this work : mixing, slacking or thinning, roasting or baking, and subjection to the air, is analogous to the work of a tile or brick-works. The advance of the oxidation can be followed by the appearance of the matter, which after baking presents a deep green color, which passes from olive green into yellow, according to the progress of calcium chromate formation. When the oxidation is completed, the mass contains : chromate of calcium, chloride of calcium, carbonate of lime and caustic lime in excess, sesquioxide of iron and the gangue, part of which is united with the lime. This mass is washed with water, by the ordinary method of lixiviation, and there is obtained a concentrated solution containing all the chloride of calcium and a small quantity only of chromate of calcium, the latter being about 100 times less soluble in water.

This solution can be used in the following ways :

1. It can be concentrated and used in preparing a new charge,

the small quantity of calcium chromate present being an assistance, or :

2. It can be used for making chromate of lead (chrome yellow), by precipitating the calcium chromate with a lead salt ; this being a very economical process for the manufacture of this color.

The mass after lixiviation, being treated with a solution of sulphate or carbonate of potash or soda, will yield chromate of potash or soda, and by the employment of sulphuric acid, the corresponding bichromates. The solutions are then filtered, to get rid of the insoluble deposits, concentrated, and crystallized.

If, instead of chromate or bi-chromate of potash or soda, chromic acid is sought, the mass after lixiviation is treated with sulphuric acid, and the chromic acid is obtained directly without any intermediate steps.

This process has the following advantages :

1. The oxidation can be effected at the ordinary temperature, thus saving expense in fuel.

2. The heavy manual labor is avoided.

3. The loss of potash and soda by volatilization and combination with the gangue is entirely avoided,

4. It is not actually necessary to use rich ores ; silicious ores can be used.

5. The intimate mixture of the material before treatment being made mechanically, the puddling is avoided, and in consequence a greater proportion of the sesquioxide of chromium in the ores is utilized.—*Mm. J. Massignon and E. Vatel. (Bull. Soc. Chem. 5, 371.)*

W. W. D.

THE ESTIMATION OF THE PECULIAR ODORIFEROUS MATTER IN SOILS.

It is known that the soil, when it has been recently wet, emits a peculiar odor, which is not disagreeable ; for instance, after a short rain. Several attempts have been made to discover the origin of this odor. These researches have established the fact that the essential principle of this odor resides in an organic compound of a neutral nature of the aromatic family, and which is carried by the vapor of water after the manner of a body possessing a feeble

tension. The odor is penetrating, almost piquant, and analogous to that of camphorated substances, and quite distinct from other known substances. In regard to the quantity of this substance, it is extremely minute, and can be regarded as being only a few millionths of a per cent.

This new principle is neither an acid nor an alkali, nor even a normal aldehyde. It is, in a concentrated aqueous solution, precipitable by the carbonate of potassium with the production of a resinous substance. Heated with potash, it develops a sharp odor similar to the resin from aldehyde. It does not reduce ammoniacal nitrate of silver. Treated with potash and iodine, it gives an abundant formation of iodoform, which, however, is a property common to a great number of substances. For the qualitative and quantitative estimation of the odoriferous matter, the following process is employed :

About 3 kilograms of the vegetable soil are mixed with sand containing a small amount of carbonate of lime and some humic substance. After having freed it from all organic debris which is visible, it is placed in a glass alembic. The soil should contain from 10 per cent. to 12 per cent. of water, at least. The alembic is placed in a sand bath, and is kept at 60 degrees for several hours. The water evaporated is condensed until about 75 cc. are distilled over. This distilled water is again rectified, so as to obtain in all about 20 cc. The odoriferous matter appears to be nearly all contained in this 20 cc. The liquid thus obtained shows an alkaline reaction ; it contains some ammonia, and reduces ammoniacal nitrate of silver. This last reaction is due to some pyridic alkali or analogue thereof and is cause for it to be distilled anew with a trace of sulphuric acid, which gives a neutral liquor deprived of all reducing action, but which preserves the odor peculiar to the soil. The 20 cc. obtained as before are subjected to two additional distillations, and in the final one only one cc. of liquid is distilled over.

The peculiar odor is intensified proportionately, as the volume of the liquid is decreased. To this one cc. is added some carbonate of potassium, pure and crystallized. The liquor is immediately troubled, and some hours are required for it to become clear again. Meanwhile there is formed upon its surface a resi-

nous ring, almost invisible, amounting at most, from 10 to 20 mg. of a matter which has not been identified with any known principle. The reactions described before, however, permits of its general character being known.—*Mm. Berthelot & Andrè. Comptes rendus, Vol. 112, No. 12, Page 598.*

H. W. W.

THE VALUATION OF ALUMINUM AND ITS ALLOYS.

The color, conduct under the hammer, cut and fracture are characteristics that, to an experienced eye, often indicate very closely the purity of commercial aluminum. Pure aluminum is white and as the impurities increase the color changes to bluish green. The purer the metal the deeper it may be cut with the chisel before it breaks. The fracture in the pure metal is finely crystalline and silky in appearance, with increasing amounts of silicon and iron this crystalline structure becomes coarser. The metal on being cast contracts and the surface is marked with fine branching needles, with increasing amounts of iron the surface is more coarsely crystalline and the contraction is less; with increasing amounts of silicon the appearance of crystallization disappears altogether. Iron deteriorates the quality of the metal more than silicon.

Aluminum is quite soluble in hydrochloric acid, caustic potash solution, Aqua Regia (HCl in excess), dilute hydrofluoric acid, very soluble in sulphuric acid, very insoluble in nitric acid. By solution in caustic potash, iron, copper and most other metals are left in the residue, but silicon is dissolved. Too much washing of the residue is liable to carry through some iron which will show in the filtrate.

1. *Silicon*.—2-4 gms. of the metal, in fine cuttings, are placed in a platinum dish with six times as much pure caustic potash and 50 cc. warm water, and covered with a platinum cover, as the action is quite violent; when solution is complete, neutralize with hydrochloric acid, evaporate to dryness, stirring occasionally, take up with hydrochloric acid and water and filter. The ignited and weighed residue must be treated with sulphuric and hydrofluoric acids for correction.

2. *Iron*.—3 gms. of chips are placed in $\frac{1}{2}$ L. flask with 50 cc. 40 per cent. caustic potash solution; when solution is complete

200 cc. of pure sulphuric acid sp. gr. 1.16 are added and the solution boiled until clear. Titrate directly into the flask with permanganate solution.

3. *Aluminum*.—2 gms. of chips are dissolved in caustic potash solution and diluted to 200 cc.; 50 cc. of this clear solution are boiled with 20 gms. of ammonium nitrate and filtered on the pump, well washed, ignited and weighed. The precipitate is granular and washes freely. The weighed precipitate is finely ground, a weighed portion boiled with water to remove alkali; another portion is fused with bi-sulphate of potassium, dissolved in water and the silica filtered, ignited and weighed. The amounts in the whole precipitate may be calculated from these results.

4. Qualitative tests may be made for other metals in the filtrates from 1 or 2.

The author is of the opinion that the silicon in metallic aluminum is in two forms, the oxidizable form being in chemical combination with the aluminum, and the unoxidizable form occurring as free silicon; the latter may be seen in the residue of a high silicon alloy dissolved in hydrochloric acid, occurring in fine silky needles of the so called graphitoidal silicon. To determine the amounts of silicon occurring in each form the author proceeds as follows: The portion insoluble in hydrochloric acid when ignited gives the weight

$$p = x (\text{Si}) + z (\text{Fe}_2\text{O}_3) + y (\text{SiO}_2)$$

after fusing with KNaCO_3 and evaporating to dryness with hydrochloric acid there is obtained a new weight q . = the total silicon as silica. Now $\Delta = q - (p - z)$ or the oxygen necessary to convert the silicon into silica; then $32 : 28 = \Delta : x$ gives the amount of the unoxidizable or graphitoidal silicon and from the total may be gotten, by difference, the amount of chemically combined silicon.—*F. Regelsberger, Ztschr. angew. Chem., 1891-360. J. E. W.*

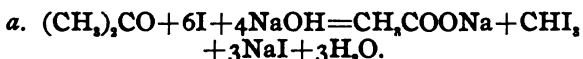
DETERMINATION OF ACETONE IN IMPURE ALCOHOL.

The alcohols used for industrial purposes usually contain from 20 to 25 per cent. of acetone, caused by the use of methylene. In the determination of this, the reaction of Lieben is generally

used, which transforms acetone into iodoform by the simultaneous action of iodine and soda. Kramer has applied this reaction to the determination of small quantities of acetone in methylic alcohol, and the author has studied and described under what conditions it can be used in determining the proportion of acetone in the denaturalizing methylenes. (Bull. Soc. Chim. 3, 595.) The method which the author has formulated for this occasion is not applicable *a priori* in the presence of ethylic alcohol. But a recent study has shown that, by taking certain precautions, it is possible to use the reaction of Lieben for the determination of acetone in denaturalized alcohols, that is, in the presence of a great quantity of ethylic alcohol.

The new method is based upon the following experiences :

1. If iodine and soda are made to act upon acetone in the presence of water, two distinct and principal reactions take place.



Under ordinary conditions, one of these reactions will predominate more or less. In the most favorable case, supposing the reaction *b* to be sensibly null, to change into iodoform CHI_3 , one molecule of acetone $(CH_3)_2CO(58)$, requires 6 atoms of free iodine $(127 \times 6 = 762)$, or for 1 gm. of acetone, 13.1 gms. iodine. But this case never occurs. In practice, the reactions *a* and *b* always coexist, and at times the equation *b* predominates to such an extent, that to transform the acetone into iodoform requires the employment of as much as 145 atoms of iodine instead of 6, or 24 times the theoretical quantity.

2. In the presence of methylic alcohol in excess, for mixtures containing 20 to 25 per cent. of acetone, it is necessary to use 13.7 atoms of free iodine for one molecule of acetone ; or 30 gms. of iodine for 1 gm. acetone.

3. Ethylic alcohol exercises upon the reaction a remarkable influence.

Alone, under the specified conditions, it will give no iodoform ; mixed with acetone, it opposes the formation of iodoform and causes reaction b to predominate.

The following experiments establish these two propositions :

a. 5 cc. of ethylic alcohol were increased to 250 cc. with distilled water. To 5 cc. of this liquor 10 cc. of binormal soda solution were added, and, after mixing, 5 cc. bi-normal iodine solution; the mixture was shaken, and immediately extracted with 10 cc. ether at 65 degrees; 5 cc. of the ether evaporated at the ordinary temperature gave no residue.

b. 5 cc. of 55.5 per cent. acetone was diluted to 250 cc. 5 cc. of this, after the addition of 40 cc. bi-normal NaOH, and 20 cc. bi-normal iodine, gave a quantity of iodoform corresponding to 55.34 per cent. acetone.

c. A liquor prepared with 5 cc. of 55.5 per cent. acetone, 5 cc. of pure ethylic alcohol, and water to make 250 cc., treated as in *b*, gave no greater quantity of iodoform than corresponds to 28.54 per cent. acetone.

4. Aldehyde favors the formation of iodoform.

d. 5 cc. of a solution composed of: 5 cc. of 55.5 per cent. acetone, mixed with 5 cc. pure ethylic aldehyde, and 240 cc. H₂O, gave, under the preceding conditions, 95.93 per cent. acetone.

5. From a mixture *M*, composed in the greater part of ethylic alcohol, without aldehyde, and containing 5 per cent. by volume of pure acetone, there were prepared with H₂O three liquors, *A*, *B* and *C*, containing 5, 10, and 25 cc. of *M* in 250 cc. After treatment of each liquor with 10 cc. NaOH bi-normal and 5 cc. bi-normal iodine, and weighing the iodoform, the following results were obtained :

	Amount of <i>M</i> Employed. cc.	Acetone Obtained. gms.	Theory. gms.
<i>A</i>	0.1	3.92 for 100 cc.	4.07
<i>B</i>	0.2	3.62 "	4.07
<i>C</i>	0.5	3.02 "	4.07

The proportion of acetone found diminishes with the increase of the proportion of alcoholic liquor. It has been established, however, that *A* gives no more iodoform, while *B* and *C* both yield it upon further treatment with iodine. For instance, to transform $\frac{0.1 \text{ cc.} \times 0.8}{20} = 0.004$ gm. acetone into iodoform, 5 cc. of bi-normal iodine, or 1.27 cc. of free iodine have been necessary; or, for 1 cc. acetone (1 mol.), 317 gms. of iodine (145 atoms).

The author operates in the following manner :

After having eliminated the aldehyde, 5 cc. of the sample is diluted to 250 cc. (A).

In a cylinder, well stoppered and graduated to 100 cc., is introduced 10 cc. bi-normal soda [2NaOH (in gms.) = 1 liter,] and 5 cc. of A. After agitation, 5 cc. of bi-normal iodine [$(2\text{I} + 2\text{KI})$ in gm. = 1 liter] is run in, and the whole well shaken. The iodoform formed is then extracted with 10 cc. ether at 65 degrees. 5 cc. of this is taken, and after evaporation, the residue is weighed. From this the acetone is calculated. For definite results, the author advises duplication, and trials with double the quantity of iodine and soda.—*M. Leo Vignon (Bull. Soc. Chim. 5, 745.)*

W. W. D.

TWO NEW ALLOTROPIC STATES OF SULPHUR.

Two new allotropic conditions of sulphur have been prepared by Engel in the following way: two volumes of a solution of hydrochloric acid containing from 25 to 30 per cent. of acid, and at a temperature of 10° , are mixed with constant stirring with one volume of the same strength of a solution of hyposulphite of soda. Chloride of sodium is precipitated and hyposulphurous acid set free. The acid in this condition possesses a sufficient stability to permit of its being filtered without coloration. Little by little the filtered liquid becomes yellow and the intensity of the coloration increases, and at the same time sulphurous acid is disengaged. When the yellow tint has become very pronounced and before the liquid has become cloudy from the precipitation of sulphur, the filtered solution is shaken with an equal volume of chloroform. The chloroform is separated in a separatory funnel and left for spontaneous crystallization. There are thus rapidly obtained some crystals of sulphur, which are absolutely different from octahedral sulphur. The sp. gr. of these crystals is 2.135. Their crystallographic nature has been studied by Friedel.*

These crystals belong to the rhombohedric type as manifested by the deportment with polarized light and crystalline measurements and are absolutely different from any other form of sulphur known.

*Comptes Rendus, Vol. 112, No. 16, p. 834.

At the moment of their preparation they are transparent and remain so for 3 or 4 hours. Then they commence to increase in volume and pass little by little into a state of insoluble amorphous sulphur. They melt below 100° . The coloration of these crystals is orange yellow and not lemon yellow as are those of octahedral sulphur and their analysis shows that they are composed entirely of sulphur.

A solution of hyposulphurous acid in HCl, prepared as directed above, when left gives a precipitate of sulphur which on cooling unites into yellow flakes. In this state, the sulphur is entirely soluble in water. Not only does it dissolve when water is added to the liquid which holds it in suspension, but when spread rapidly upon a filter, it preserves *in toto* its solubility in water. The solution in water is rapidly decomposed, giving the ordinary amorphous sulphur.

The explanation of the formation of these two allotropic forms of sulphur appears to be the following: hyposulphurous acid in the conditions before mentioned undergoes a progressive decomposition into sulphurous acid and sulphur. This sulphur is now in the atomic state or at least in a state but little removed therefrom. Little by little the sulphur after separation is condensed to the molecular form. This condensation takes place in two different manners according as the sulphur has been dissolved or not, from the liquor in which it is generated, by chloroform. In the first case the sulphur passes at once into the crystalline form. In the second case it is transformed into amorphous sulphur soluble in water before it attains its maximum condensation.—*Comptes Rendus, Vol. 112, No. 16, p. 866.*

H. W. W.

DETERMINATION OF WATER IN SUPERPHOSPHATES.

The author repeated Brinbaum's experiment upon the influence of temperature on monocalcium phosphate, using a chemically pure phosphate having the composition

CaO	22.36 per cent.
P ₂ O ₅	56.67 "
H ₂ O	21.53 "

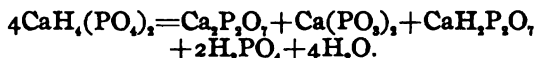
containing 0.014 per cent. of free phosphoric acid. 3.59 gms. were taken and dried at 100 degrees.

The loss of water in 10 hours was 1.83				
"	"	"	20	" 2.46
"	"	"	30	" 5.21
"	"	"	40	" 6.32
"	"	"	50	" 6.43

This last loss, viz., 6.43 per cent., remained constant. $\text{CaH}_4(\text{PO}_3)_2 \cdot \text{H}_2\text{O}$, therefore, loses its water of crystallization at 100 degrees, but only in 50 hours. The calcium phosphate thus obtained formed opaque crystals, non-hygroscopic, which contained

CaO	24.02 per cent.
P_2O_5	60.74 "
H_2O	15.00 "

It is slowly soluble in 200 parts of water, and if dried for more than 20 hours at a temperature above 105 degrees, a slight decomposition takes place, until by increasing the heat to 200 degrees the change is expressed by the equation :



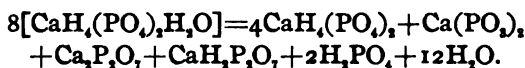
When water in the proportion of 1 : 200 acts upon such dried calcium phosphate, the monocalcium phosphate, the monocalcium pyrophosphate and the phosphoric acid dissolve while the pyro- and meta-calcium phosphate are undissolved. In performing this experiment, the monocalcium phosphate was dried in a platinum capsule at 105-120 degrees, dissolved in water at 15 degrees in the proportion of 1 : 200, the free and total phosphoric acid were determined in the filtrate, in part directly by means of uranium acetate, and in part with molybdate solution, and then the calcium oxide was determined. In the part insoluble in water was determined the phosphoric acid and calcium oxide.

5 gms. monocalcium phosphate were dried for one hour at 200°. The loss of water was 7.20 per cent., or, in other words, 50.4 per cent. of monocalcium phosphate had been decomposed. The dried substance was mixed with a liter of water, and after being shaken for one hour, the liquid was filtered through a weighed filter, dried at 120 degrees, and weighed. The residue was dissolved in aqua regia, the excess of acid driven off, and the solution diluted to 250 cc. The analysis gave

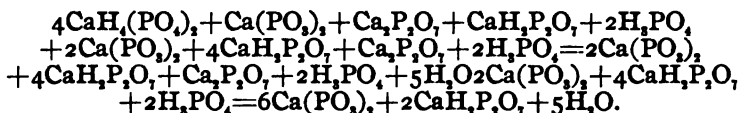
	36.81	per cent.	CaO,	and	62.20	P ₂ O ₅ ,	or by calculation,
	37.12	"	"	"	62.88	"	"
	23.15	per cent.	pyro- and calcium meta-phosphate				
(theoretical)	22.42	"	viz.,	12.6	Ca ₂ P ₂ O ₇		
				9.82	Ca(PO ₃) ₂		

The free phosphoric acid in the aqueous solution of the mono-calcium phosphate was determined by titration with decinormal potash, using methyl orange for an indicator and 6.66 per cent. P₂O₅ (=9.2 H₃PO₄ — calculated 9.72 per cent.) was found. Titration of the total acid in the solution by means of uranium acetate will always give lower results than the molybdenum method, owing to the mono-calcium pyrophosphate present. This may be converted into mono-calcium orthophosphate by boiling with a few drops of nitric acid.

The percentage of mono-calcium phosphate decomposed by drying for an hour, at different temperatures, varies from 1.84 at 150° to 48.20 at 200°. The chemical changes which take place during the desiccation may be expressed by the following equations. Drying at 200 degrees for one hour—



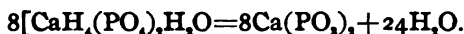
further drying at 200 degrees, gives



If the pyrophosphate is completely decomposed at 210 degrees, we have



Briefly the changes may be all summarized in the reaction expressed



—*Julius Stocklasa Chem. News 63-100-114-122 (Zeitschrift anal. Chemie).*

A. H. W.

AMMONIUM SELENITE AS A REAGENT FOR THE DETECTION OF THE ALKALOIDS.

Lafon called attention to (June, 1885) ammonium sulposelenite as a reagent for morphine and codeine. He prepared it by dissolving

1 gm. ammonium selenite in 20 cc. concentrated sulphuric acid. The author has studied the reagent further in its reactions with other alkaloids, placing small portions of the alkaloids in his experiments upon watch glasses set upon white paper. The following is the table he has prepared :

Atropine. No coloration.

Aconitine. No immediate coloration ; after 20 minutes, a very slight rose-color.

Berberine. Greenish yellow, becoming successively very brown rose at the margins and violet in the middle ; half an hour afterwards entirely vinous red, which lasts for three hours.

Brucine. Reddish or rose color, becoming pale orange ; half an hour after, an amber color, and no deposit.

Caffeine. No distinct coloration. At end of three hours, the liquid was reddish, and there appeared a slight deposit.

Cinebonnie. Nothing.

Cinebonidine. Nothing.

Cocaine. After half an hour, no decided coloration or precipitate. After three hours the same reaction as caffeine.

Curarine. Slight violet coloration ; after some time reddish. No red deposit at the end of three hours.

Delphine. Slightly reddish coloration, passing into a violet red. No ppt. at the end of three hours.

Digitaline. No immediate color. Yellowish after half an hour. After three hours a reddish deposit.

Eserine. Lemon yellow color, turning to orange. Three hours afterwards the color was paler.

Morphine. Bright greenish blue ; half an hour after maroon yellow and no deposit. After three hours, the liquid maroon brown, no red deposit.

Narcotine. Bluish color, becoming violet and then reddish. After half an hour a fine reddish color and no ppt. After three hours a small red deposit.

Narceine. Yellow-green color, becoming brownish, and after half an hour reddish. Afterwards a red deposit, which is very distinct in two or three hours.

Papaverine. Bluish color ; the liquid becoming bottle-green, dirty yellowish green, violet blue, then red. A small bluish deposit.

Pilocarpine. Nothing.

Solanine. Canary yellow, and then brownish. After half an hour, a rose colored ring, and after three hours the liquid becomes violet red.

Saponine. Yellowish, becoming slightly reddish. (Reaction not distinct.)

Senegine. Light, dirty yellow. After three hours, liquid reddish.

Veratrine. Indistinct yellowish color, sometimes with a green tone. After half an hour yellow. After three hours, deposit red and liquid yellowish. (Reaction indistinct.)

—A. J. Ferreira de Silva, *Chem. News*, 63, 291, (*Comptes Rendus* 112, 1266.)

A. H. W.

NOTES.

—*The Meeting of the Chemical Section* of the A. A. A. S. in Washington this year was unusually successful in the number and character of papers presented and the number of working chemists who were present and took an active part. Vice-President Kedzie chose as the subject of his address, Alchemy, and his remarks were addressed chiefly to the modern alchemists. Among others he paid his respects to Prof. Crookes and his protyle. His remarks upon this subject were in excellent taste, but very searching, and full—if we may be allowed the expression—"a long felt want." Dr. Norton filled the Secretary's chair—full. The committee on Spelling and Pronunciation of Chemical Words presented a final report, and was discharged. Dr. Howe was, however, authorized to keep on the lookout for any new words that may turn up. It is only fair to state here that if the work of the committee shall be found to have value, credit should be given for the most part to Dr. Howe, who has had principal charge of the work, and who has given a great deal of time and study to the preparation of the reports. With Dr. Prescott in the President's chair, Dr. Wiley as General Secretary, and all the Washington men to see that we had a good time, it was a great week for the chemists.

—*A Resolution was offered this year* in the Chemical Section of the A. A. A. S., providing for the appointment by the chair of a sectional committee of three persons to devise a plan for facilitating the business of the section and for adding to the value of the discussions upon the papers presented. Many of the papers presented before the section are necessarily long, and are read at length, requiring sometimes nearly an hour's time, and frequently twenty to thirty minutes. Even the most patient chemist tires of these papers unless he is specially interested in the subject. It is proposed : 1, to group the papers, so as to have those relating to one branch of the subject come together as far as possible ; 2, to make copies of each paper by the neostyle or mimeograph, and distribute them before the meeting, so that they need not be read in full, and so that the discussion may be more valuable ; 3, to have the discussion led in each case by some person or persons appointed by the Chairman.

If the committee is to accomplish anything, it will be necessary for those who intend to present papers to communicate with the Sectional Secretary for the Rochester Meeting, Dr. James Lewis Howe, long enough in advance to allow of the preparation of copies and their distribution to members. Where it is at all practicable, these copies should be prepared by the members themselves and sent to Dr. Howe for distribution.

There are always papers presented which for various reasons would not be ready in time to be treated in the manner proposed, and these would have to be read in full, as is now done; but if the proposed plan can be applied to but half a dozen of the papers read, it will certainly be of benefit. Papers intended for subsequent publication in this journal may be put in type, reprints furnished, and publication of the paper withheld until after the meeting, *provided sufficient time is allowed the printer*.

Any suggestion for the benefit of this committee may be sent to the Chairman, Dr. Springer.

The members of the committee are—

Dr. Alfred Springer, Box 621, Cincinnati, O., Chairman, and Vice-President of the Section for the Rochester meeting.

Dr. James Lewis Howe, Polytechnic Society, Louisville, Ky., Secretary for the Rochester meeting.

Prof. S. A. Lattimore, Rochester University, Rochester, N. Y.

—*The American Chemical Society* held a meeting at Washington on August 17 and 18. The conference committee appointed by this and the other chemical societies, after much talking, finally came to an agreement. This is, in substance, that the New York members shall form a local section of the Society and give up the name to the national organization. Whether this plan will prove successful will of course depend upon the men who are to be placed at the head of the national organization. It is therefore important that chemists from all parts of the country shall attend the next meeting of the American Chemical Society, to be held probably in October, and of which due notice will be given, to assist in perfecting the organization and making it a society which shall fitly represent American chemists.

THE

Journal of Analytical AND Applied Chemistry.

THE DETERMINATION OF MOLYBDIC AND TUNGSTIC ACIDS.

BY EDGAR F. SMITH AND ROBERT H. BRADBURY.

The gravimetric methods proposed for the estimation of these acids have been almost wholly confined to their combinations with mercury and lead (Berzelius, Gibbs, Zettnow and Chatard). It occurred to us that possibly other molybdates and tungstates might serve equally well, or, perhaps even better, for this purpose. To this end, a series of experiments was made with the barium, calcium, strontium, lead, silver, cobalt, bismuth, and cadmium salts. Solutions containing known amounts of pure sodium molybdate and tungstate were employed for this purpose.

I. PRECIPITATION OF THE ACIDS AS BARIUM SALTS.

Barium Molybdate.—This salt separates from cold solutions of sodium molybdate upon the addition of barium chloride. It dissolves in acids without a residue. When the acid solution is digested for some time, upon an iron plate, the liquid acquires a bluish color. Barium molybdate dissolves more readily in a dilute ammonium nitrate solution than in pure water.

A determination of the solubility of barium molybdate in water was made by the Victor Meyer method, and showed that one part of the salt was soluble in 17,200 parts of water at 23 degrees.

To ascertain what results could be obtained in the quantitative way with this salt, a definite volume of the sodium molybdate solution, containing 0.1144 gm. of molybdenum, was diluted with water to 200 cc. and boiled. A boiling solution of barium chloride was added to it. When the precipitate had subsided, it was filtered and thoroughly washed with hot water. The filter was ignited apart from the precipitate. The ignition was quite gentle,

as a red heat occasions loss, and incorrect results follow. Two determinations conducted in this manner gave :

	Molybdenum Found.	Molybdenum Calculated.
1	0.1124 gm.	0.1144 gm.
2	0.1124 "	

An examination of the filtrates showed the presence of molybdenum. In the subsequent determinations, the precipitate, after long boiling, was allowed to subside. The liquid was cold before it was filtered. Cold water was employed for washing purposes.

	Molybdenum Found.	Molybdenum Calculated.
1. 0.1134 gms.	}	0.1144 gms.
2. 0.1132 "		
3. 0.1138 "		
4. 0.1136 "		
5. 0.1140 "		
6. 0.1141 "		
7. 0.1143 "		

The filtrates from these precipitates, except those of 1 and 2, contained no molybdenum.

Barium Tungstate.—This is a heavy, white precipitate. It is, apparently, unaffected by dilute acids in the cold, but upon the application of heat it is decomposed with the separation of yellow tungstic acid. Like barium molybdate, it is more soluble in water containing ammonium nitrate than in pure water.

In the quantitative determinations, the solution of sodium tungstate, about 200 cc. in volume, was boiled, and a dilute solution of barium chloride added. The barium tungstate subsided rapidly, and was filtered. It was washed with hot water. Like barium molybdate, it is readily separated from the filter. The latter, after being moistened with ammonium nitrate, was reduced to ash upon the crucible lid.

	Tungsten Found.	Tungsten Calculated.
1. 0.1389 gms.	}	0.1396 gms.
2. 0.1390 "		
3. 0.1391 "		
4. 0.1390 "		

The filtrates did not show tungsten.

II. PRECIPITATION OF THE ACIDS AS STRONTIUM SALTS.

Strontium Molybdate.—This salt resembles barium molybdate in appearance; it is insoluble in water, and more easily decomposed by ignition. It is not well suited for the determination of molybdic acid. One part of strontium molybdate is soluble in 9600 parts of water at 17 degrees C.

The following results were obtained by precipitating in a manner perfectly analogous to that followed with the barium salt:

Molybdenum Found.		Molybdenum Calculated.
1.	0.1129 gms.	} 0.1144 gms.
2.	0.1144 "	
3.	0.1123 "	

The variation in results indicates that the process is of no value. The addition of alcohol to the solution, with a view of rendering the strontium molybdate more insoluble, gave results that were too high. Impurities were, no doubt, included in the precipitate.

The same unsatisfactory conditions were observed with strontium tungstate.

III. PRECIPITATION OF THE ACIDS AS CALCIUM SALTS.

Calcium Molybdate.—Calcium chloride does not produce a precipitate in a cold, dilute solution of sodium molybdate. A white, pulverulent precipitate, slightly soluble in water, insoluble in alcohol, appears immediately upon the addition of the latter, or when the solution is boiled. The addition of $\frac{1}{3}$ volume of acetic acid to the solution prevents the precipitation. Calcium molybdate is infusible.

In the first determinations of molybdic acid as calcium molybdate the treatment was similar to that pursued with the barium salt. In fact the two were often conducted side by side, digested equal lengths of time, washed with the same volume of water and ignited similarly. Molybdenum was invariably found in the filtrates, yet the results were high. In order to produce complete precipitation, the addition of calcium chloride and one-third volume of alcohol, in the cold, was tried, but the precipitate then falls in such a finely divided state, that filtration is impossible.

The following treatment at last gave a successful determination. The solution of the sodium molybdate, 150 cc. in volume, was brought to boiling, and calcium chloride added, causing the immediate formation of a white precipitate. The boiling was continued until the precipitate had become granular and the supernatant liquid was clear. The heat was now removed, the solution allowed to cool, one-third volume of strong alcohol added, and the whole allowed to stand some time, usually over night. The precipitate was washed with dilute alcohol (1 : 3). By this treatment the filtrate obtained was nearly or quite free from molybdenum, but the high results, observed in the aqueous precipitations, continued.

Upon exposing the precipitate to a red heat in a platinum crucible, a fall in weight was observed. This continued upon subsequent ignitions until a figure, nearly corresponding to that calculated, was reached ; the weight then remained constant even on heating for long periods.

A quantity of calcium molybdate, obtained by the preceding process, from a solution in which there was 0.1144 gms. of molybdenum, was ignited gently in a platinum crucible for fifteen minutes. It weighed 0.2459 gms., corresponding to a quantity of molybdenum greatly in excess of the proper amount. After ignition for fifteen minutes, at a strong yellow heat, over a good burner it weighed 0.2387 gms., corresponding to molybdenum 0.1145 gms. Further ignition for a like period at a yellow heat produced little or no change, as it weighed 0.2386 gms. After being ignited at the same intensity for an hour it weighed 0.2386 gms. The following results were obtained by igniting the precipitated calcium molybdate at a high heat for fifteen minutes, and then weighing :

Molybdenum Found.	Molybdenum Calculated.
1. 0.1145 gms.	} 0.1144 gms.
2. 0.1140 "	
3. 0.1141 "	
4. 0.1140 "	

Calcium Tungstate.—This salt resembles the preceding compound in many respects, but it cannot be employed for quantita-

tive purposes. The results obtained vary between wide limits, and are altogether untrustworthy.

IV. PRECIPITATION OF THE ACIDS AS LEAD SALTS.

Lead Molybdate.—This is a white, granular precipitate. When moist it is soluble in nitric acid and sodium hydroxide. After ignition, by which it transiently assumes a yellow color, it is apparently unaffected by these reagents.

In the determination of molybdic acid in this form, we can simply confirm the statement of others,* in every particular. We weighed the lead salt in porcelain crucibles. The results obtained are :

Molybdenum Found.		Molybdenum Calculated.
1.	0.1143 gms.	} 0.1144 gms.
2.	0.1144 "	
3.	0.1137 "	

The precipitate is adherent in character, fixing itself tenaciously to glass and rubber.

Lead Tungstate.—This is a white, curdy-flocculent and finely divided precipitate. Like the molybdate, it is perfectly insoluble in water. We can amply corroborate Chatard's statement in regard to the difficulty of filtering this salt, having lost a large number of determinations by this peculiarity. The turbidity of the filtrate is much reduced, and altogether prevented by the addition of ammonium nitrate, in which reagent the salt is totally insoluble, even when the ammonium salt is present in the quantity of 20 gms. in 150 cc. of water.

The results we present below were obtained by precipitating the boiling sodium tungstate solution with lead acetate, and adding varying quantities of ammonium nitrate.

	Tungsten Found.	Ammonium Nitrate.	Tungsten Present.
1	0.1397 gms.	2 gms.	0.1396 gms.
2	0.1384 "	2 "	0.1396 "
3	0.1388 "	3 "	0.1396 "
4	0.1396 "	4 "	0.1396 "
5	0.1390 "	5 "	0.1396 "

*Zettnow, Jahresbericht, 1867, p. 267; Chatard, Am. Journ. Science and Arts, Vol. I, 3d series, p. 416.

The filtrates of two—2 and 3—were slightly cloudy, and showed traces of tungsten when examined.

It is probable that the difficulties connected with this method can be removed by the addition of ammonium nitrate both in the precipitation, and to the wash-water. We observed, however, that when the precipitate, with the ammonium nitrate from the wash-water remaining in it, was dried with the filter, the latter was charred, and the precipitate adhered to it in such a manner that complete separation could not be effected.

V. PRECIPITATION OF THE ACIDS AS SILVER SALTS.

Silver tungstate and molybdate are immediately precipitated upon the addition of silver nitrate to solutions of sodium molybdate or tungstate. Silver tungstate is more finely divided and difficult of filtration than the molybdate. The latter is a white, curdy precipitate, resembling silver chloride. It is somewhat soluble in water. It dissolves freely in nitric acid, potassium cyanide, and ammonium hydroxide. It becomes purple in color upon ignition. It fuses to a clear yellow liquid at a very low heat. On cooling the salt is still soluble in potassium cyanide. Silver tungstate is more yellow in color, is less soluble in water, fuses less readily, and when ignited is darker purple in color.

These salts are not suited for the determination of either acid, because of their solubility and ready decomposition upon ignition.

VI. PRECIPITATION OF THE ACIDS AS CADMIUM SALTS.

Cadmium Molybdate.—This salt is heavy and granular in appearance. It is insoluble in water. It is soluble, in a moist condition, in ammonium hydroxide, the acids, and potassium cyanide. The molybdate is soluble in acids after ignition. It loses acid upon ignition with filter paper.

In the quantitative experiments, the precipitation was made with a pure cadmium nitrate solution. The volume of the sodium molybdate solution did not exceed 200 cc. The precipitate was boiled and filtered, both while hot and after becoming cold. It was also washed with either hot or cold water. Experience showed that it was best to filter the cadmium salt through a

weighed porcelain Gooch crucible. After drying, it was carefully ignited in the same.

Molybdenum Found.		Molybdenum Present.
1.	0.1148 gms.	} 0.1144 gms.
2.	0.1149 "	
3.	0.1147 "	
4.	0.1143 "	

Cadmium Tungstate.—This precipitate is finely divided, but gave no difficulty in its filtration. It resembles the molybdate in solubility, although after ignition it does not dissolve in acids. They decompose it to a large degree. The precipitations were made in the same manner as with the molybdate. A porcelain Gooch crucible was used in filtration after ignition.

Tungsten Found.		Tungsten Present.
1.	1.396 gms.	} 0.1396 gms.
2.	1.391 "	

It seems likely that an indirect determination of molybdic and tungstic acids can be made, when they occur together in solution, by dividing the latter into two equal portions, in the one precipitating and weighing the acids in the form of cadmium salts; in the other, precipitating them similarly, but dissolving the well washed precipitate, consisting of cadmium molybdate and tungstate, in potassium cyanide, electrolyzing the solution, weighing the cadmium deposit, and making the appropriate calculations. This, however, remains to be tried practically.

The bismuth salts were found to be insoluble in water, but no quantitative experiments were made upon them.

Cobalt molybdate does not form in cold solutions, either when they are dilute or concentrated. When a concentrated solution of sodium molybdate was mixed with cobalt nitrate and then boiled, small quantities of a bluish white precipitate appeared. This redissolved when the liquid became cold.

Cobalt tungstate is violet in color, and appears immediately on the addition of cobalt nitrate to a solution of sodium tungstate. Its precipitation is very incomplete from dilute solutions.

THE ELECTROLYTIC PRECIPITATION OF IRON.

BY EDGAR F. SMITH AND FRANK MUHR.

Iron can be completely precipitated from an ammoniacal tartrate solution, in the cold, by a current generating not more than 3 cc. of electrolytic gas per minute. The deposit is bright and steel-like; it is also very adherent.

Experiment 1. A solution of ferric ammonium sulphate, containing 0.1610 gms. of metallic iron, was mixed with one gm. of tartaric acid, and 10 cc. of ordinary aqua ammonia; a current generating 2.5 cc. of electrolytic gas per minute acted upon the solution, diluted to 150 cc. for a period of twenty hours. The bright metallic deposit of iron weighed 0.1650 gms.

Experiment 2. The conditions were similar to those in 1. The current, however, gave 3 cc. of electrolytic gas per minute. The iron deposit weighed 0.1652 gms.

It will be noticed that the two deposits were 0.0040 gms., and 0.0042 gms. in excess of the theoretical amount of metallic iron. After being carefully weighed, they were heated in an air-bath, at 160 degrees, for an hour. They sustained no loss, indicating that occluded gas could not well have caused their increased weight.

When the iron was dissolved in dilute, cold sulphuric acid a strong odor of hydrocarbons was perceptible. After complete solution, and gentle warming, until the hydrocarbon odor had disappeared, cold water was added to the liquid, when it was titrated with potassium permanganate. The iron found in each of the experiments equaled 0.1610 gms., thus agreeing accurately with the required quantity.

Additional experiments were performed under varying conditions; these showed that while the iron always contained carbon, the amount of the latter was not constant, but that it varied very considerably.

It is possible to separate iron from aluminium by the current, when they are present together in solutions of the above description.

Nickel, cobalt, zinc, copper and cadmium were precipitated electrolytically from similar solutions and quantitative results obtained. None of these metals, however, carried down carbon.

THE ELECTROLYTIC SEPARATION OF MERCURY FROM COPPER.

BY EDGAR F. SMITH AND ARTHUR W. MCCAULEY.

The separation of mercury from copper, in the electrolytic way, has been tried and described.* The method, however, is not complete. The separation is only perfect when the quantity of copper present in the mixture does not exceed 20 per cent. of the mercury. We have given further study to this problem, and have found that by careful adjustment of the current, it is not only possible to separate these metals completely when present together in equal amounts, but even when the quantity of copper is twice that of the mercury. In brief, the separation is as readily and accurately made as that of any other metal, e. g., zinc from mercury. Furthermore, the presence of zinc, nickel, or other metals, in no wise influences the separation of the mercury from the copper.

The conditions of experiment and the results may be tabulated as follows :

	Mercury Present, in Grams.	Copper Present, in Grams.	Zinc Present, in Grams.	Nickel Present, in Grams.	KCN, in Grams.	Total Dilution.	Current in cc. of OH Gas per Minute.	Mercury Found.	Difference in per cent. from Theory.
1	0.1018				3	135 cc.	1 cc.	0.1018	
2	"	0.1250			"	"	"	0.1018	
3	"	"			"	"	"	0.1020	+0.19
4	"	"			"	"	1.1 cc.	0.1015	-0.29
5	"	"			"	"	"	0.1012	-0.58
6	"	"			"	"	1 cc.	0.1019	+0.09
7	"	"			"	"	"	0.1012	-0.58
8	"	.2500			3.7	"	0.13 cc.	0.1014	-0.39
9	"	"			"	"	"	0.1017	-0.09
10	"	"			"	"	"	0.1008	-0.98
11	"	"			"	"	"	0.1017	-0.09
12	"	.0500	.0500		3	130 cc.	1.3 cc.	0.1020	+0.19
13	"	"	"		"	"	"	0.1021	+0.20
14	"	"	"		"	"	"	0.1013	-0.49
15	"	"	"		"	"	"	0.1015	-0.29
16	"	"		.0500	"	"	1.15 cc.	0.1014	-0.39
17	"	"		"	"	"	"	0.1016	-0.19

The time allowed for the precipitation of the mercury in the

*Smith & Frankel, Am. Chem. Journ., XI, p. 264; Frank. Inst. Journ., April, 1889. This Journal 3, 254.

preceding experiments varied from 18 to 20 hours. Cold water was employed for washing purposes. The deposits were dried upon a moderately warm iron plate. The precipitated mercury did not show the presence of any of the other metals when it was examined for them. The filtrate from the deposit in No. 10 showed a trace of mercury. This probably was due to the removal of particles of mercury in the process of washing. This last operation had better be carried out without interruption of the current where extreme accuracy is desired.

UNIVERSITY OF PENNSYLVANIA,
JUNE 10, 1891.

THE OXIDATION OF THE MINERAL CHALCOCITE BY THE ELECTRIC CURRENT.

BY EDGAR F. SMITH AND D. L. WALLACE.

It has been shown elsewhere (Ber. 23, 2276; Jr. Frank. Inst. 180, 145) that representatives of the various classes of metallic sulphides are so decomposed in alkaline solution by the electric current, that their entire sulphur content is changed to sulphuric acid (K_2SO_4). The only exception to this statement was the mineral chalcocite (Cu_2S). A series of experiments made upon the mineral, during the past year, has led to its complete decomposition, so that at present it may be claimed that all sulphides can be completely oxidized in the electrolytic way. The very purest chalcocite, which could be obtained, was used in the decompositions.

Experiment 1. 0.1068 gms. of finely divided chalcocite, and 35 gms. of caustic potash, were acted upon in a nickel crucible, 2 inches wide and $1\frac{3}{4}$ inches high, with a current generating one ampere of electrolytic gas per minute, for a period of forty minutes. The current was reversed for a few minutes, before its final interruption. The crucible contents, after cooling, were extracted with water, the solution filtered from the insoluble oxides, acidulated with hydrochloric acid, and then precipitated with a solution of barium chloride. The pure barium sulphate weighed 0.1618 gms., equivalent to 20.80 per cent. of sulphur. The residue, insoluble in water, was dissolved in acid and examined for sulphur, but none was discovered.

Experiment 2. 0.1153 gms. of material, treated as in 1, gave 0.1756 gms. of purified barium sulphate, equal to 20.91 per cent. of sulphur.

Other specimens of chalcocite were oxidized in the same manner; the results showed that this mode of oxidation was complete.

The differences, which will be noted on comparing the procedure adopted in the decomposition of this particular sulphide with the course answering for all the other sulphides, are: the use of a larger quantity of alkaline hydroxide, and a longer period of exposure to the action of the oxidizing agent. Chalcocite collects in little nodular masses when it is thrown upon the melted alkali, and in order that they may be separated, and every particle of material oxidized, it was necessary to extend the period of oxidation to forty minutes. Complete oxidation of the sulphur was not obtained in a shorter space of time. The addition of ferric oxide to the finely divided chalcocite did not prevent it from collecting in masses. Therefore, as already stated, recourse was had to more prolonged oxidation.

A portion of the same chalcocite, that gave the two quantitative results already mentioned, was oxidized with nitric acid. The sulphur found equaled 21.00 per cent. It will be observed that the electrolytic results agree quite well with this.

UNIVERSITY OF PENNSYLVANIA,
June 10, 1891.

THE PROPERTIES, USES, AND PROCESSES OF PRODUCTION OF ALUMINUM.*

BY ALFRED E. HUNT, S.B., PRESIDENT OF THE PITTSBURGH
REDUCTION COMPANY.

The metal aluminum has certainly not been "damned by faint praise." On the contrary, from my experience as the president of an aluminum manufacturing company which has been endeavoring for the past two years and over to sell the commercially pure metal in the markets, and to introduce it into the arts and manufactures of the country, I have to state to you as my conviction that one of the two chief difficulties encountered, and which to-day retards and restricts the wider use of the metal, is the extravagant, erroneous, and in many cases mischievously

*A lecture before the Society of Arts, Massachusetts Institute of Technology, February 12, 1891.

misleading, statements which have been made as to the properties of the metal, which have received wide circulation, not only through the daily newspapers, but, I am sorry to add, through many technical and scientific journals as well. The other difficulty is the almost equally widespread, and, so far, equally extravagant and misleading, series of claims made by the inventors of processes for the manufacture of aluminum at remarkably low prices.

I shall endeavor in this lecture to correct some of these fallacies as to the properties of the metal, and also, in describing the minerals in which the metal occurs and the methods of reduction which have been practiced, to explain the principal difficulties which have thus far been encountered. I shall also venture a prophecy as to the success of cheaper methods of manufacture of aluminum in the future.

PURE AND IMPURE ALUMINUM.

Some of the erroneous statements regarding aluminum have had their origin in the fact that commercial aluminum is never chemically pure, and that until within the past eight years nearly all the aluminum of which the properties had been described had at least 4 per cent.—in many cases 6 or 8 per cent.—of impurities. These materially altered the characteristics from those of the purer metal, with not over 2 per cent. or at most 3 per cent. of impurities, which is ordinarily sold in the markets to-day.

The impurities almost always found in aluminum are silicon and iron. These two impurities are almost the only ones found in the electrolytically deposited metal, considerable amounts of any others being accidental and due to carelessness in manufacture. In fact, I hope to be able in the near future to say that the impurity consists in the single one, silicon, as we have already made many hundred pounds of aluminum, with only a trace of iron present, and tons of metal with less than one-tenth of one per cent. of iron.

The silicon present in aluminum exists in two forms, one seemingly combined with the aluminum, as combined carbon exists in white pig-iron, and the other in an allotropic graphitoidal modification. These two forms of silicon seem to exert somewhat differ-

ent effects by their presence in the aluminum ; the combined form of the element rendering the metal much harder than the graphitoid variety. The combined silicon ordinarily preponderates, being from 55 to 80 per cent. of the total silicon in the average metal of between 98 and 99 per cent. purity made by the Pittsburgh Reduction Company.

For many purposes, the purest aluminum cannot be so advantageously used as that containing 3 or even 4 per cent. of impurity, as the pure metal is very soft and not so strong as the less pure. It is only where extreme malleability, ductility, sonorousness, or non-corrodibility is required that the purest metal should be chosen. We shall probably find that for most purposes a small percentage of other elements than silicon and iron are advantageously added in producing hardness, rigidity, and strength—constituents that will not detract from the non-corrodibility of the metal as much as do these natural impurities that come from the ore and apparatus—additions that will give the aluminum a better color and greater strength and hardness, with proportionately less sacrifice of malleability, ductility, etc.

COLOR OF ALUMINUM.

Pure aluminum is white, with a decided bluish tint. This becomes much more marked upon exposure, when a thin film of white oxide on its surface prevents further tarnishing from the air, but seems to give, by contrast to the metal as a background, an enhanced bluish tint. I am sorry to hear my good wife report this color as giving a decidedly pewtery appearance to the spoons and forks which we have had in almost constant daily use, for comparison with silver, during the past year and a half. The oxide which gives this decided blue tint may be removed by immersion in a dilute solution of hydrofluoric acid, and then rubbing with chamois skin saturated with petroleum.

No one should expect the color of silver in aluminum—especially of silver of the markets, which is given a decided yellow tinge with copper ; for the natural color of aluminum is different, and the addition of copper, although making the metal a yellower white, does not entirely change its natural bluish-white tint. The addition of small percentages of silver, chromium, manga-

nese, wolfram, or titanium, undoubtedly improves the color of aluminum, making it nearer to that of silver.

ACTION OF HEAT ON ALUMINUM.

Aluminum melts at about 1300 degrees F., but becomes pasty at a temperature of about 1000 degrees F., and indeed loses its tensile strength and very much of its rigidity at a temperature of 400 to 500 degrees F., although this loss of strength is only while the metal is kept at the high temperature. It serves as an annealing operation, and reduces permanently only the higher tensile strength produced by cold rolling or otherwise cold working the metal. Aluminum does not volatilize at any temperature ordinarily produced by the combustion of carbon, even though the high temperature be kept up for a considerable number of hours. It, however, absorbs a very large amount of occluded gases under such treatment. In the high temperature of the electric furnace, it is claimed that there is considerable volatilization of aluminum, and that small buttons of the metal have been found in and on the linings of the furnace. The Cowles people, however, have never been enabled to collect and commercially produce pure aluminum by their electric furnace, for the reason that the metal rapidly oxidizes into alumina. It has only been by protecting the reduced metal with an alloy of either iron or copper that they have succeeded at all in retaining the reduced aluminum.

Under heat, the coefficient of linear expansion of $\frac{3}{8}$ in. round aluminum rods of 98.50 per cent. purity is .0000206 per degree centigrade between the freezing and boiling points of water; that of iron being .0000122, tin .0000217, copper .000017182. Multiplying this factor by $\frac{5}{9}$ to reduce it to the Fahrenheit scale, we have .0000115, or an expansion of .00115 feet on 100 feet of aluminum raised 1 degree F. from 32 degrees. It is probable that the coefficient of expansion of alloys of aluminum is very close to that of tin.

The specific heat of aluminum is 0.2143, water being taken as 1. The metal follows the general rule of metals, its specific heat being inversely as the atomic weight.

By the method of Weidemann and Franz, taking silver as 100 and copper as 73.6, unannealed aluminum of 98.50 per cent. purity

has a coefficient of thermal conductivity of 37.96; and the same wire annealed, 38.87. In the same scale, tin has a heat conductivity of only 14.50, iron 11.90, steel 11.60, and lead 8.50. From this it is evident that, next to silver, copper, and gold, soft annealed aluminum is the best conductor of heat.

ELECTRICAL PROPERTIES OF ALUMINUM.

It also stands next to silver, copper, and gold, as a conductor of electricity. One yard of annealed aluminum wire of 98.50 per cent. purity, .0325 inch in diameter, at 14 degrees C. has .05484 of an ohm resistance, a yard of pure copper wire of same section having a resistance of .0315 of an ohm. The electrical conductivity of silver being taken at 100, and copper at 90, pure annealed aluminum has an electrical conductivity of about 50. These facts, taken into consideration with the lightness of the metal as compared with silver, gold, and copper, are already leading to a quite extensive use of aluminum in electrical apparatus.

Pure aluminum, and indeed the electrolytically made commercial aluminum, with less than $\frac{1}{5}$ of 1 per cent. iron, regularly put upon the market to-day, exhibits no appreciable polarity. Such metal has many advantages for compass boxes, or for cases for electrical apparatus where non-magnetic properties are desired.

MECHANICAL PROPERTIES OF ALUMINUM.

The fracture of aluminum shows ordinarily hexagonal crystals, although the pure metal is very tough, and in breaking, by bending backward and forward, often appears distinctly fibrous in fracture. The lack of rigidity and hardness which the metal exhibits is a serious obstacle to its adaptability for many purposes, although both stiffness and hardness are very much increased by the addition of a few per cent. of impurities or alloy, and are especially improved by cold-hammering, cold-rolling, drop-forging, or the like. For castings for surveying instruments, pure aluminum would be especially adapted were it not for its softness and lack of rigidity. It can be safely stated as a general rule that the purer the aluminum, the softer and less rigid it is.

Pure aluminum is, when properly treated, a very malleable and ductile metal. It can readily be rolled into sheets five ten-thousandths of an inch thick, or be beaten into leaf nearly as thin as

gold leaf, or be drawn into the finest of wire. Pure aluminum stands third in the order of malleability, being exceeded only by gold and silver; and in the order of ductility, seventh, being exceeded by gold, silver, platinum, iron, softest steel, and copper. Both malleability and ductility are greatly impaired by the presence of the two common impurities, silicon and iron.

Aluminum can be rolled or hammered cold, but the metal is most malleable at between 200 and 300 degrees F., and should be heated to this point for rolling or breaking down from the ingot to the best advantage, and even then considerable power is required, fully as much as for hot-rolling of hard steel of similar section, although not nearly as much draft can be placed upon the rolls as in hot-rolling hard steel. Like silver and gold, aluminum stiffens up remarkably by working it, increasing a great deal its hardness and its tensile strength, and decreasing its malleability and ductility; it requires to be frequently annealed. As compared with cold-rolling soft steel, it has been found practicable to give aluminum about the same reduction in each pass as the steel; the aluminum requiring on the average five annealings where the steel requires but three.

By hardening the metal by rolling, forging, drop-forging, stamping, drawing, etc., it may be turned out very rigid, and will then answer excellently for purposes where the annealed metal would be entirely too soft, too weak, or lacking in rigidity or elasticity. Especially is this true of aluminum alloyed with a few per cent. of titanium, copper, iron, silicon, or the like. The alloys do not show their increased hardness to anything like their maximum extent in castings, and, I am sorry to say, not at all in proportion to the increased brittleness. But when these castings are drop-forged, rolled, hammered, or drawn down, with only sufficiently frequent annealings to prevent the metal from cracking, the increased hardness shows up in a remarkable degree. These properties have already become not only the subject of a considerable number of letters patent, but also of established uses in the arts, and will, in future, add enormously to the applicability of the metal.

ANNEALING ALUMINUM.

To anneal aluminum, a low and even temperature should be

maintained in the muffle—just such a temperature as will show an even, red heat in a piece of iron or steel placed in the muffle, when viewed at twilight or on a dark day. The aluminum itself, however, should not appear at all red at this temperature. A ready test of this temperature is that the metal has been heated enough to char the end of a pine stick, which will leave a black mark on the plate as it is drawn across it. When the metal has acquired this temperature, it should be taken from the furnace and allowed to cool gradually. Very thin sections may be annealed by placing into boiling water and either allowing to cool with the water or taking out to cool gradually. Of course it is possible to anneal to any degree by lowering the temperature to which the metal is heated below that specified by means of suitable appliances.

WELDING AND SOLDERING ALUMINUM.

Aluminum can be easily and readily welded by the apparatus of the Thompson Electric Welding Company.

Until very lately the lack of methods for successfully soldering and hardening aluminum were two of the greatest drawbacks to its introduction for many purposes. I am glad to be able to say to you, however, that both of these difficulties, I believe, have lately been successfully overcome. I have already outlined to you the method of alloying pure aluminum with a few per cent. of hardening-metal, and cold-rolling or otherwise working, as being ways out of the difficulty of its softness. The exhibitions of soldered metal will show you that aluminum can now be successfully soldered. These results were obtained by the use of the blowpipe and with ordinary hard or soft solder, or with pure zinc, or with an alloy of zinc and aluminum, as the soldering metal. The novelty, which has just been covered by letters patent in one successful case, is in the soldering salt, which allows the solder to flow freely on the surfaces to be united.

CASTING ALUMINUM.

Sound castings of aluminum can be readily made in dry sand molds. The aluminum should not be heated very much beyond the melting point; otherwise it seems to absorb gases, which remain in the metal, preventing sound castings. In small quanti-

ties the metal can be best melted in plumbago crucibles; but in large quantities it can be more economically melted in a reverberatory furnace with alumina or magnesia brick sides and alumina bottom. The furnace should have a tap-hole for drawing off the liquid metal into carbon-lined ladles. In no case need the metal be covered with a flux to assist in the fusion or to form a covering of slag. In fact, owing to the metal's lightness, the presence of any flux will tend to unsoundness, due to particles of it becoming entangled in the castings, while impurities may perhaps be added to the metal by the action of the flux on the lining of the melting vessel. The molten metal flows readily, and not much larger gates are needed than for brass. The shrinkage of $\frac{15}{64}$ inch per foot, which aluminum has, is considerably more than that of brass, which is about $\frac{3}{32}$ inch per foot. The shrinkage can be reckoned ordinarily as about 2.26 per cent. of the length of the mold. Wooden patterns made for brass, to give equivalent castings of aluminum, should be given three or four thick coatings of shellac.

RESISTANCE OF ALUMINUM TO CORROSION.

As to the corrodibility of aluminum, a great deal has been printed that is not correct. In the first place, aluminum is acted upon by the atmosphere, especially by moist atmosphere, and more especially still by moist salt atmosphere. The metal becomes covered by a very thin, almost imponderable, coating of oxide on the surface exposed to the atmosphere, which seems to protect it from further oxidation. This coating is so thin as often to hardly interfere with any polish, and it does not materially change the weight of the metal. It does, however, increase the bluish tint of the metal, as before explained, and gives it a leadish color. As compared with most metals, pure aluminum, under ordinary circumstances, withstands the action of wind and weather exceedingly well; and many uses to which the metal is now being successfully applied are based upon this fact. The presence of silicon in aluminum materially detracts from its power to withstand corrosion due to atmospheric influences. Metal with 4 or 5 per cent. of silicon very soon collects a thick coating of oxide upon it, if severely exposed. The fact that pure aluminum is not acted upon by boiling water or by steam has led to its use as a

packing or gasket in steam connections, where lead and similar metals have been rapidly cut out (especially where the water contained notable amounts of sulphur acids), as in parts of steam and water pumps and difficult steam joints. The New York Steam Company have found it a very satisfactory way of packing their leaky steam joints to put in first a layer of aluminum wire, without attempting to calk it much, adding another ring of the softer, but more especially corroded, lead on the outside, which can be calked into place, making the joint steam-tight.

Aluminum containing sodium is rapidly acted upon by hot water, the sodium being eaten out, leaving the aluminum spongy and porous. Aluminum is unaffected by either concentrated sulphuric or nitric acids, Unfortunately, however, these commercial acids almost always contain some little hydrochloric acid, which rapidly corrodes the aluminum, the chloride of aluminum first formed being changed into sulphate or nitrate, the free hydrochloric again acting more violently as it attacks the metal in a nascent state.

Aluminum is not acted upon by carbonic acid, or carbonic oxide gases, nor by sulphuretted hydrogen except at a red heat; but it is a peculiarity of the metal in a melted condition to absorb large quantities of these gases, quite a portion of which is again excluded as the metal cools. But enough is left in the case of the sulphide to emit strong odors of the sulphuretted hydrogen which has been occluded and imprisoned in the metal in cooling. This fact is a strong obstacle to a sulphide method of reduction of the metal, where the sulphuretted hydrogen evolved would strongly impregnate the metal for a long time, even after several meltings.

ALUMINUM FOR CULINARY AND SURGICAL PURPOSES.

Pure aluminum has neither taste nor odor, nor is it corroded by any substances ordinarily used in culinary operations, and it seems, therefore, especially adapted for cooking utensils. For spoons, forks, and large dishes, the metal also is useful, although its color can be improved, and the metal made more rigid, by a slight addition of copper.

Aluminum is less acted upon than is tin or copper or silver by salt water, and even by such solutions in vinegar as the metal is liable to be subjected to in ordinary culinary vessels. The salts

of tin or copper thus dissolved are very poisonous ; but not only are the aluminum salts that are formed less in amount, but the acetate of aluminum formed resolves itself on boiling into either an insoluble sub-acetate or into pure alumina, neither salt having either taste or injurious toxic action. For these reasons, quite surely aluminum will have a large future for cooking utensils. A cooking skillet of aluminum has been in service for a year in my own household.

Aluminum is found to withstand the action of organic secretions better even than silver, and for many forms of surgical instruments, tracheometer tubes, suture wires, and the like, and for forms for holding false teeth, the metal is already receiving very wide use. Many surgeons are having their instrument cases made of aluminum, it having the advantage that they can safely be washed clean with antiseptic solutions. It may be well for me to say, here, however, that perspiration in handling polished aluminum does tarnish the metal, and that aluminum, like other metals, cannot retain a high polish with frequent handling. The natural acid solvent for aluminum is hydrochloric acid. Solutions of the caustic alkalies, chlorine, bromine, iodine, and fluorine rapidly corrode aluminum. Ammonia gas has very little action on the metal, except to turn it a gray color. Strong aqua-ammonia has a slight solvent action upon it.

OTHER PHYSICAL PROPERTIES OF THE METAL.

The specific gravity of aluminum, of course, is one of its most striking properties—a property on which many brilliant “castles in the air” have been built. It runs from 2.56 to 2.70; structural steel is 2.95 times as heavy, copper 3.60 times, ordinary high brass 3.45 times, nickel 3.50 times, silver 4 times, lead 4.80 times, gold 7.70 times, and platinum 8.60 times as heavy. Many uses have been suggested for the metal due to its lightness ; one is for the entire framework of air ships. Now as there are many strong woods which have a specific gravity below 1, and which are, therefore, about one-third the weight of aluminum, and as woods can be selected that will by no means require three times the section of aluminum to give equal strength for frames, I do not quite understand where the applicability of aluminum for this purpose comes in. Of course, in many cases a much thinner sheet or

smaller section of aluminum could be used than of wood ; but for purposes where rigidity as well as lightness is required, the parts of air ships could be made much better of wood than of aluminum. I will confess that as aluminum is a favorite metal of mine, I am loth to see it subjected to the rude falls to which, I fear, it will be endangered if attempts are made to build air ships of it.

Pure aluminum is very sonorous, and varying qualities of sound are given by its different alloys. Unfortunately, just the right shape for an aluminum bell has not yet been discovered. The ordinary forms give out anything but an agreeable sound.

THE STRENGTH OF ALUMINUM.

Cast aluminum has about the ultimate strength of cast iron in tension, but under compression it is comparatively weak.

The following table gives the average results of many tests of aluminum, having about the following composition : Aluminum, 97 to 99 per cent.; silicon, graphitic, 0.10 to 1 per cent.; silicon, combined, 0.90 to 2.80 per cent.; iron, 0.04 to 0.20 per cent.

Tension Tests.	Castings.	Sheet.	Wire.	Bars.
Elastic limit per sq. in., lbs. . . .	6,500	12,000	16,000 to 30,000	14,000
Ultimate strength per sq. in., lbs. . .	15,000	24,000	30,000 to 60,000	28,000
Reduction of area	15%	35%	60%	40%

Compression tests (in cylinders with length twice the diameter) :

Elastic limit per sq. in.	3,500 lbs.
Ultimate strength per sq. in.	13,000 lbs.

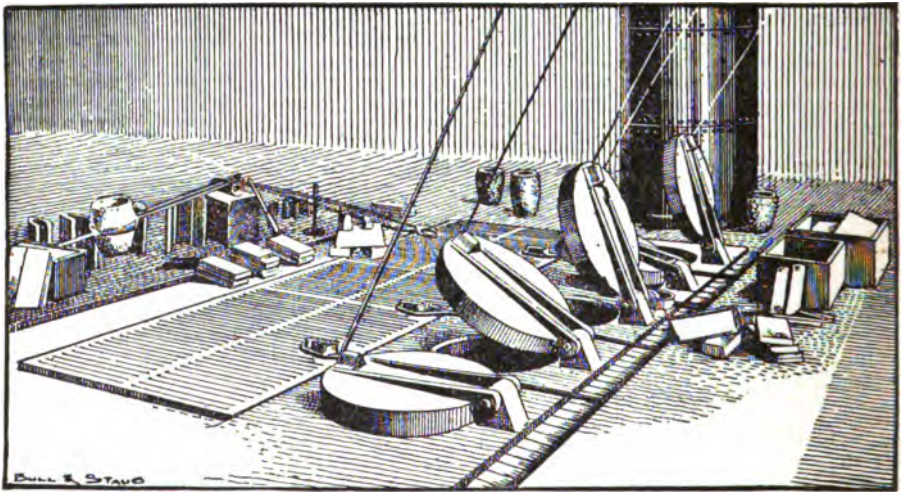
The modulus of elasticity of cast aluminum is about eleven million ; cold drawn aluminum wire, about nineteen million ; aluminum sheets, about thirteen million.

Under transverse test pure aluminum is not a very rigid metal. An inch square bar of good cast iron, supported on knife edges 4 feet 6 inches apart and loaded in center, will readily stand 500 pounds without a deflection of over 2 inches. A similar bar of aluminum would deflect over 2 inches with a weight of 250 pounds, although the aluminum bar would bend nearly double before breaking, while the cast-iron bar will ordinarily break before the deflection has gone very much beyond 2 inches. Aluminum to withstand strains, and especially to have good elasticity, should be alloyed with a few per cent. of impurities and cold rolled, or

otherwise worked cold. In this way it can be made to be nearly as strong and elastic as mild steel, section for section, and weight for weight will be much more rigid.

ALLOYS OF ALUMINUM AND COPPER.

Aluminum and copper form two series of valuable alloys; the aluminum bronzes, ranging from 2 to 12 per cent. aluminum with copper, and the copper hardened aluminum series, with from 2 to perhaps 15 per cent. of copper with the aluminum. The alumi-



MELTING HOLES — PITTSBURGH REDUCTION COMPANY'S PROCESS.

num bronze series are already beginning to assume an important position in the arts, and I believe will very largely replace brass and other bronzes, and for some purposes take the place of steel. By adding 8 to 12 per cent. of aluminum to copper, we obtain one of the densest, finest grained, and strongest metals known—a metal having a remarkably good ductility as compared with its tensile strength. A 10 per cent. bronze can readily and uniformly be made in forged bars, with 100,000 pounds per square inch tensile strength, with 60,000 pounds elastic limit per square inch, and with at least 10 per cent. elongation in 8 inches, and aluminum bronzes can be made to meet a specification of even 130,000

pounds per square inch and 5 per cent. elongation in 8 inches. Such bronzes have a specific gravity of 7.50, and are of a light yellow color. The 5 to 7 per cent. aluminum bronzes have from 8.30 to 8 sp. gr., and a handsome yellow color. They readily give 70,000 to 80,000 pounds per square inch tensile strength, with over 30 per cent. elongation in 8 inches, and with an elastic limit of over 40,000 pounds per sq. inch. It will probably be alloys of the latter character that will be most used, especially for marine work. The fact that 5 to 7 per cent. bronzes can be rolled or hammered at a red heat, proper precautions which can readily be secured being taken, will add greatly to their use. Metal of this character can be worked in almost every way that steel can, having for its advantage greater combined strength and ductility, and much greater power to withstand corrosion. By far the best results have been obtained by using the purest aluminum and purest copper. The presence of silicon in aluminum alloys makes a harder bronze, but one of much less comparative ductility and malleability. The presence of iron weakens and very seriously interferes with the value of bronze. Tin also is disadvantageous. The presence of zinc in the aluminum bronze is not so deleterious; in fact, it makes the best aluminum bronzes, much better than those having tin in them.

The Cowles and Heroult people, who by their methods manufacture aluminum bronze by direct reduction, have claimed that the bronze directly reduced was more homogeneous and better than that made by melting together copper and pure aluminum. Careful experiments made in this matter, however, have failed to show this claim to be true. From my experience, I entirely agree with Professor Richards, who, in his excellent work, says: "Two specimens containing nothing but aluminum and copper in like proportions will be identical, no matter how they are produced." As it is far easier, and at present cheaper, to produce a bronze with less iron and silicon by using pure aluminum of less than 2 per cent. of these impurities, which with pure copper will give less than one-fifth of 1 per cent. impurity in the bronze, the advantage is certainly on the side of the use of pure aluminum, melting it with pure copper, so far as quality is concerned.

The aluminum in bronzes lowers the melting point of the copper

at least 100 or 200 degrees. The melting point of 10 per cent. aluminum bronze is somewhere in the neighborhood of 1700 degrees F.

WORKING ALUMINUM BRONZE.

Aluminum bronze is among the hardest of the bronzes, and hardens upon cold-working considerably. This hardness, however, can readily be lowered by annealing at a red heat and plunging into cold water. Aluminum bronze can readily be worked in a lathe, and the chips cut clean, smooth, and long, and do not clog the tool. Aluminum bronze is a remarkably rigid metal under transverse strain, being much more rigid than ordinary brass, or even gun bronze. Under compression its strength, although rather low in elastic limit compared to its ultimate compressive strength, is still much higher than that of any of the other bronzes, and there is a long period of gradual compression before finally giving way, making it peculiarly a safe metal under compression.

Aluminum bronze has excellent anti-friction qualities owing to its fine grain texture and peculiar smooth and unctuous though hard surface, which resists abrasion remarkably. Attention has already been called to the anti-corrosive qualities of aluminum bronze; and as its electrical conductivity is better than that of brass, it is peculiarly well adapted for commutator bars in dynamos. It can be brazed and soldered nearly as well as brass.

CASTING ALUMINUM BRONZE.

Sound, clean castings of aluminum bronze can be safely and regularly made, either in sand molds or against chills, if the proper precautions are taken to avoid: first, oxidation; second, contamination from scum or a cinder composed of oxide of aluminum with a little copper in it; third, depressions, cracks, or strains due to shrinkage; fourth, the shutting in of gas into the castings. The first trouble, oxidation, is due to heating the metal too hot in the plumbago crucible. The copper should not be heated much above its melting point before the aluminum is added, which at first absorbs a great deal of heat and rapidly thickens the metal, the aluminum being rapidly immersed in the copper to prevent its oxidation. Great care should then be taken in again bringing

the metal up to the liquid condition, and the metal should be frequently stirred; for it suddenly heats up by the reaction of the alloying of the two metals, and, unless precautions are taken, will soon bring the temperature up to a white heat, where oxidation will seriously injure the bronze. The metal should have a cover of powdered charcoal to prevent oxidation, but with no other flux over its surface.

The second trouble, contamination from the scum, can be avoided by pouring from the melting furnace or pot into a hot ladle or pouring basin large enough to hold all the metal necessary to fill the mold and to allow the metal to pour out from the bottom of such a receptacle after giving sufficient time to allow the scum to come to the surface. A skim-gate should also be provided for each mould.

The third difficulty is caused by a peculiar red-shortness just after solidification, and also a contraction at solidification which causes the metal to either tear apart or yield and cause depressions in the casting at more favorable spots, if any great resistance is experienced by the metal in contraction. This difficulty is overcome by giving bountiful allowance for the contraction, which can be done in several ways, each best adapted for varying conditions. The cores should be made of a yielding character, using resin or other suitable substance with coarse sand, that will yield to slight pressure. Unyielding iron core rods should be dispensed with as far as possible. "Green" sand cores will give good results in some cases. Other expedients to gain the same ends will be easily suggested by skilled molders.

The troubles due to shrinkage are avoided by having the "risers" or "feeding heads," with flaring openings, large in section, often larger than the castings they are intended to feed, and if necessary refilling the feeding heads, in some cases several times over. In this way the casting will solidify first, drawing metal to supply its shrinkage from the still fluid riser having a level higher than the casting itself, so that the metal will flow down into it. The gates to the mold should be sufficient in number and so arranged that they can be filled with the metal as cold as it will pour and give full castings. The considerable amount of

scrap occasioned by the large sectioned risers can be remelted without loss of aluminum, and, indeed, is improved in quality by the process of remelting.

To prevent the shutting in of gas into the castings, dry sand should be used, and the molds should be well vented by the ordinary precautions taken by founders for this purpose. Although it requires skill and experience to successfully carry out the conditions outlined above, sound, clean castings, even of the most difficult sections of aluminum bronze, can be made regularly, and with no more wasters than with ordinary brass, and without the difficulty of a copious liberation of gas at the moment of solidification, as is the case with steel. In fact, aluminum bronze, with its low pouring temperature, is especially applicable for massive and heavy castings.

ALLOYS WITH SMALL PERCENTAGES OF COPPER.

The alloys of aluminum with copper in proportion of from 2 to 15 per cent. have already been incidentally referred to. Copper, I believe, is one of the best hardeners of aluminum. The maximum proportion that can be added before the metal becomes too brittle to work depends largely upon the purity of the aluminum. If it contains several per cent. of silicon, it becomes very brittle with 5 per cent. of copper; but with pure aluminum it is still forgeable, with difficulty, with 15 per cent. of copper. Even very small percentages of copper added to pure aluminum decrease the blue color of the metal and give a more pleasing yellow-white color to it.

Proportions of a few per cent. of copper added to pure aluminum decrease the shrinkage of the metal and give alloys that are especially adapted for art castings. The remainder of the range, from 15 per cent. copper up to over 85 per cent., give crystalline and brittle alloys of no use in the arts, and of a grayish-white color, up to 80 per cent. where the distinctly yellow color of the copper begins to show itself.

There is said to be an alloy of 50 per cent. copper and 50 per cent. aluminum, which is malleable. I have, however, been unable to discover any such alloy in experiments which I have

made in this direction, all of the alloys being very crystalline and brittle.

ALUMINUM WITH IRON AND STEEL.

Aluminum combines with iron in all proportions. None of the alloys, however, have proved of value, except those of small percentages of aluminum with steel, cast iron, and wrought iron. So far as experiments have yet gone, other elements can be better employed to harden aluminum than iron, and its presence is regarded as entirely a deleterious impurity, to be avoided if possible.

The addition of from $\frac{1}{3}$ pound to 2 pounds of aluminum to a ton of steel gives the advantage of quieting the metal in the mold and producing ingots with much sounder tops, so that the scrap due to crop ends is materially lessened, a saving which much more than pays for the cost of the aluminum added. The amount to be added varies with the character and condition of the steel. With well-melted steel, low in carbon, the proportion of from $\frac{1}{3}$ to $\frac{1}{2}$ pound to the ton seems to give the best results; any larger proportion making the metal pipe and causing excess of crop-end scrap. If the steel be "wild" in the ladle, full of occluded gases, too hot, or oxidized, a larger proportion of aluminum can be advantageously added. Mr. R. A. Hadfield says, I think correctly, that the influence of aluminum appears to be like that of silicon, though acting more powerfully. The same writer, together with Professor H. M. Howe and Mr. Osmund, claims that an addition of aluminum does not lower the melting point of steel. In this my own experience agrees; nor do I believe that aluminum increases to any great extent the fluidity of the steel. So far as my experience goes, steel, with an addition of one-tenth per cent. of aluminum, seems to solidify in the molds fully as quickly as steel without the addition of the aluminum. Aluminum seems to take the oxygen out of steel very much in the same way that manganese does, but I am not aware of any advantages gained by using the more expensive aluminum for this purpose.

The addition of aluminum in quantities of from 2 to 3 pounds per ton is of advantage where the steel is to be cast in heavy ingots which will receive only scant work. Here it seems to increase the ductility as measured by the elongation and reduction of area

of tensile test specimens, without materially altering the ultimate strength.

The question as to whether additions of aluminum prevent segregation of impurities in large castings of steel, is still an unsettled one ; but I may say that it is now being carefully investigated.

In steel castings the benefit from the use of a small percentage of aluminum, ordinarily in the proportion of from 2 to 3 pounds per ton, has become widely recognized, and it is being generally used.

The additions of aluminum are almost always made by throwing the metal, in pieces weighing a few ounces each, into the ladle, as the steel is pouring into it. In cast iron, from 2 to 5 pounds of aluminum per ton is put into the metal as it is being poured from the cupola or melting furnace. To soft gray No. 1 foundry iron it is doubtful if the metal does much good, except, perhaps, in the way of keeping the metal melted for a longer time ; but where difficult castings are to be made, where much loss is occasioned by defective castings, or where the iron will not flow well, or give sound and strong castings, the aluminum certainly in many cases allows of better work being done and stronger and sounder castings being made, having a closer grain, and hence much easier tooled. The tendency of aluminum is to change combined carbon to graphitic, and it certainly lessens the tendency of the metal to chill. Aluminum in proportions of 2% and over materially decreases the shrinkage of cast iron.

The effect of aluminum in wrought iron is not very marked in the ordinary puddling process. It seems to add somewhat to the strength of the iron, but the amount is not of sufficient value to induce the general use of aluminum for this purpose.

The peculiar property of aluminum in reducing the long range of temperature between that at which wrought iron first softens and that at which it first breaks down and becomes fluid, is taken advantage of in the well-known Mitis process. It is for this that aluminum is most used in wrought iron at present.

ALUMINUM AND OTHER METALS.

With the exception of lead, antimony, and mercury, aluminum

unites readily with all metals; and many useful alloys of aluminum with other metals have been discovered within the last few years. I venture to prophesy the finding of many more in the near future, as more systematic attempts are made to study the use of aluminum with other metals and metalloids. Of many of these useful improvements that are now subjects of letters patents, for obvious reasons, I will say nothing. The useful alloys of aluminum so far discovered are all in two groups, the one of aluminum with not over 15 per cent. of other metals, the other of metals containing not over 15 per cent. of aluminum; in the one case, the other metals imparting hardness and other useful qualities to the aluminum, and in the other the aluminum giving useful qualities to the other metals.

The alloy of a few per cent. of silver to aluminum to harden, whiten, and strengthen the metal, gives a metal especially adaptable for many fine instruments, tools, and electrical apparatus, where the work upon the tool and its conveniences are of more consequence than the increased price due to the addition of the silver. The silver lowers the melting point of aluminum and gives a metal susceptible of taking a fine polish and making fine castings.

More or less useful alloys have been made of aluminum with zinc, bismuth, nickel, cadmium, magnesium, titanium, chromium, manganese, and tin—these alloys all being harder than pure aluminum; but it is by combinations of these metals, with additions perhaps of copper, lead, and antimony, that alloys of most useful value have so far been discovered. Some are with additions of only 1 to 2 per cent. of aluminum.

The addition of from 5 to 15 per cent. aluminum to type metal composed of 20 per cent. antimony and 80 per cent. lead makes a metal giving sharper castings and a much more durable type.

To ordinary brass, the addition of aluminum gives superior strength and better anti-corrosive qualities. Some very marked and valuable qualities have been discovered in the use of aluminum with zinc for various purposes.

The modifications of pewter, Britannia, white metal, Delta metal, and the like, with additions of aluminum, have shown very

useful qualities, and will add very considerably to the demand for aluminum in the near future.

CLAY AS A SOURCE OF ALUMINUM.

Evidently contrary to the understanding of the case by many people who have written us with brilliant claims of rich mines, aluminum has never been found in nature in the metallic state; and yet the general statement made by Professor Richards is true, that "there is no other metal on the earth so widely scattered, and that occurs in such abundance." This statement, however, has been interpreted by the public to the effect that therefore all these varied minerals containing aluminum are equally applicable as ores from which to extract the metal; especially have they considered that clays, silicates of aluminum, are the specially chosen ores for the production of aluminum. A consideration of the comparative constituents of clay with those of the minerals given below shows the disadvantage of the richest of clays, as aluminum ores, as compared with the richer and purer oxides, fluorides, and sulphates, which minerals are now used as ores of aluminum.

Bauxite ($\text{Al}_2\text{H}_2\text{O}_3$), soft and granular; with 50 to 70 per cent. oxide of aluminum and with only a few per cent. of accidental impurities besides the water of hydration.

Corundum (Al_2O_3), very hard and crystalline, specific gravity 3.909.—With 93 per cent. alumina and ordinarily very free from impurities, but so hard and crystalline, and withal so valuable for other purposes, as not to be at present used as an aluminum ore.

Diaspore ($\text{Al}_2\text{O}_3\text{H}_2\text{O}$), hard and crystalline; specific gravity, 3.4.—With 65 to 85 per cent. alumina and ordinarily very pure.

Cryolite ($\text{Al}_2\text{F}_6\text{NaF}$), specific gravity, 2.9.—With 40 per cent. aluminum fluoride and 60 per cent. sodium fluoride.

Aluminite ($\text{Al}_2\text{SO}_4\text{H}_2\text{O}$), specific gravity, 1.66.—Containing some 30 per cent. of alumina in a condition to be cheaply purified by solution, filtration, and roasting.

Gibbsite ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$), stalactitic, specific gravity, 2.4.—Containing about 65 per cent. alumina.

In comparison to these, the clays vary from tri-basic silicates of alumina to pentacid silicates, minerals with at best 65 per cent. alumina and 35 per cent. silica; while the more common clays contain from 50 to 70 per cent. silica and only from 50 to 35 per

cent alumina. Pure kaolin contains 39 per cent. alumina, carrying about 20 per cent. aluminum, with 40 per cent. silica, and 14 per cent. water. It has a formula of $\text{Al}_2\text{Si}_2\text{O}_5\cdot 2\text{H}_2\text{O}$. Now silica is much easier reduced than alumina, and by all the methods of reduction this large percentage of silica must be separated from the alumina before the reduction is commenced, else a large percentage of energy used in reduction will be expended in reducing a troublesome impurity, instead of in reducing the alumina to aluminum. The true value of clay as an ore of the metal is evident, therefore, in comparison with the richer and purer ores that have only accidental amounts of iron and silicon, up to perhaps 10 per cent., to be removed before being submitted to the reducing operation.

There seems to be one fact favorably prominent, however, in the prospect of fat clays like the kaolins being used as aluminum ores—that is, that concentrated cold sulphuric acid dissolves the alumina out of most clays, leaving the silica insoluble. Although this fact has not yet, to my knowledge, been made use of on a commercial scale, still in the future, when there is a large demand, this method may make clays available as ores of aluminum.

PREPARING ALUMINUM ORE FOR REDUCTION.

Bauxite is the mineral most used at present for the manufacture of alumina, and it probably will continue to be the most economical ore, for the reason that it is soft, easily ground and easily decomposed, to separate the impurities of silica and iron. The mineral occurs in great abundance in the South, in Tennessee, Virginia, North and South Carolina, Georgia, Alabama, and also Arkansas. Very pure bauxites can be laid down in quantities in Pittsburgh at a cost of between \$9 and \$10 per ton, and with only the cost of mining and transportation can be put on cars nearest the mines in many cases at a cost of less than \$2.50 per ton.

The general method of purification of the ore is to calcine the bauxite with just sufficient sodium carbonate to form sodium aluminate ($\text{Al}_2\text{O}_3\cdot 3\text{Na}_2\text{O}$). The temperature must be kept below the melting point (the aluminate being formed at a temperature lower than the melting point of the mixture), else silicate of aluminum is formed. The mass is well stirred to insure the com-

plete displacing of all the carbonic acid and the combination of the sodium carbonate with the alumina. A ready test of the completion of the reaction is that portions taken from the mass no longer effervesce and evolve carbonic acid upon treatment with acid. The incinerated mass is taken out of the furnace, ground and lixiviated with hot water, which takes the sodium aluminate into solution, leaving the silica and iron insoluble. The clear supernatant sodium aluminate solution is siphoned off, and the alumina is precipitated with carbonic acid gas. This forms sodium carbonate, which remains in solution, while the alumina settles out to the bottom of the tank. This is afterwards washed with hot water and dried.

The same general method of treatment is applicable to the aluminum oxide minerals for their preparation; the difficulties to overcome being in grinding the minerals, because of their hardness and the formation of the sodium aluminate at a low enough heat to prevent the sodium silicate forming. It may be that these minerals had best be taken into solution as sulphates, and thereafter treated as the native sulphates by a red heat to drive off the sulphuric acid, leaving pure alumina as a residue. With proper apparatus to condense and save the sulphuric acid, such processes may not be excessively expensive. However, neither this method of manufacture of the sulphates from clays or from native oxides, nor the method of manufacture of alumina from the sulphate by roasting, have so far found favor commercially in comparison with the soda carbonate fusion method for the preparation of the oxide. The sulphate of aluminum melted with sulphur gives off sulphuric acid gas and transforms the alumina into sulphide. This reaction has been made available in one of the methods of manufacture of aluminum from sulphide by the aid of electricity; the sulphide being afterwards decomposed by electrolysis.

COMPOUNDS OTHER THAN ALUMINA FROM WHICH ALUMINUM
HAS BEEN REDUCED.

Aluminate of soda is made from cryolite by the incineration of finely ground cryolite with an intimate mixture of chalk or finely ground carbonate of lime, with enough ground coke to keep the mixture porous. Soluble aluminate of soda is formed; insoluble

fluoride of lime remains as a waste product, together with carbonic acid which is evolved. The precipitation of the alumina from the aluminate of soda is carried on by the same method as previously described.

Aluminum sulphide, a yellow, infusible salt, containing 36 per cent. aluminum, is produced from alumina by the reaction of carbon bisulphide at a high heat in the presence of carbon. It is also prepared, as explained, by the fusion of aluminum sulphate in the presence of sulphur. It is a rather unstable compound, being decomposed by standing in moist air into alumina, with the evolution of sulphuretted hydrogen.

The chloride of aluminum was for a long time the chief salt from which the metal was produced, for the reason that it had been found that metallic sodium reduced the metal from this salt the easiest. For a long time the only practical way of cheapening the manufacture of aluminum by this method was to cheapen the manufacture of sodium and reduce the expense and improve the quality of the aluminum chloride. This proved a difficult task.

The salt varies from pure white, when pure, through the yellows to a brick red when largely contaminated with ferric oxide. It is produced by the action of chlorine gas upon an incinerated mixture of alumina with tar or some oil that will, on burning out during the incineration, leave its coke in intimate mixture with the alumina. The double chloride of aluminum with sodium is produced if a supply of salt is added to the mixture and it is treated with chlorine gas. The expense and difficulties connected with the manufacture have proven very large, and the chlorine produced has to be very carefully made to keep it free from iron. The difficulties connected with the generation and use of chlorine gas on a commercial scale are found to be very great and the deterioration of the apparatus to be very serious.

The native fluoride of aluminum and sodium, the mineral cryolite, has been used in several processes as the ore for the production of aluminum. It, however, contains too much silicon and oxide of iron to make pure metal; for, as before said, in all the methods so far devised, or which seem likely to be devised in the future, the agents that serve to reduce the alumina to a metallic

state will surely reduce all the silicon and iron from their oxides that may be present at the same time or rather previous to the reduction of the alumina. Pure aluminum fluoride (Al_2F_6) is produced by the action of sulphate of aluminum on cryolite, sulphate of soda being the by-product, according to M. Grabau. Aluminum fluoride can also be produced by the action of hydrofluoric acid on alumina. It is not such an expensive or difficult salt to prepare as the chloride, and is the compound from which aluminum is produced in many of the later and more successful processes. Metallic sodium reduces the fluoride of aluminum with the same facility with which it acts upon the chlorine compounds.

METHODS OF ALUMINUM MANUFACTURE.

Aluminum cannot be reduced from its oxide by the aid of carbon as a reducing agent, because the temperature to which the intimate mixture of the solid carbon and the alumina has to be raised can only be attained by the highest heat of an open-hearth furnace or in the electric furnace—a temperature at which the aluminum reduced cannot itself be accumulated into a molten liquid mass, and can only be retained by cloaking it with a more stable metal like iron or copper. It is for this reason that the Cowles Electric Smelting and Aluminum Company are not able in their electric furnace to manufacture commercially pure aluminum, nor the Heroult people to manufacture the metal from their process of reduction, where they electrolyze pure molten alumina, which requires a high electrically produced heat to melt the oxide. None of the other salts are susceptible of being reduced by carbon at much lower temperature than the outside, so far as yet discovered.

Debarred from using carbon as the reducing agent under the ordinary conditions which make it the practicable and economical reagent in most metallurgical operations, the advantages of other stronger reducing agents have been carefully tried. So far only one has proven commercially available, although there are many other agents capable of reducing the metal from its oxide. Metallic sodium reduces the metal from its chloride or from its fluoride salts with ease. Methods based upon the use of sodium as the reducing agent have until lately given not only the purest but the cheapest aluminum. These methods, however, of late, have

been succeeded by the cheaper and more direct processes of electrolysis of some of the aluminum salts or of the pure oxide.

THE HISTORY OF ALUMINUM PRODUCTION.

So far as history informs us, Wöhler in 1827 first reduced aluminum chloride to metallic aluminum by the aid of metallic potassium as the reducing agent. The metal was a dry powder in a finely comminuted state; it was very impure, and was only a metallic curiosity. Deville, twenty-seven years later, in 1854, was the first to produce the metal in any quantity, or with any degree of purity.

It is curious to note that the first pure aluminum made was by electrolysis; both Bunsen and Deville reduced the double chloride of aluminum and sodium by electricity generated by galvanic batteries. But as at that time the dynamo was still a machine of the future, electrolysis was soon abandoned for the sodium process by the successful concerns in the manufacture of the metal, although continued experimental efforts were made with electricity from that time to this. The first aluminum made in 1855 was valued at \$90 per pound. In 1857, with the development of the sodium method of reduction, the price was lowered to from \$28 to \$32 per pound. In 1860, the price was again lowered to about \$17 per pound, and from 1862 to 1887 the price ranged from \$12 per pound upward, according to purity. In 1887 the price was reduced to one pound sterling per pound avoirdupois; and it was at this price that the first metal made was sold by the new concerns built during that year. In 1889 the Pittsburgh Reduction Company reduced the price to \$2 per pound. As the English works of the Pittsburgh Reduction Company commenced in 1890 to sell the metal in England at five shillings (\$1.21) per pound, I presume that future writers will record a further drop in the price of the metal in 1891.

About 1857 the famous works at Salindres were established, which were under the proprietorship of Pechiney & Company for many years, and, until within the past three years, enjoyed not only the reputation of making the best, but the largest, amount of aluminum produced in the world. The care and skill shown, and the ingenious devices and precautions taken by the firm to prevent impurities in the metal by the cumbersome and expensive

sodium process in which there were so many opportunities for the addition of impurities, were worthy of the highest praise. In 1860 Sir I. Lowthian Bell, with a brother, started works in Newcastle-on-Tyne, which were abandoned in 1874. They manufactured by the sodium process. From 1874 until 1882 the French company at Salindres was the only concern making pure aluminum.

In 1882 Webster organized the "Aluminum Crown Metal Company" at Hollywood, near Birmingham, England, and by cheapening the production of aluminum chloride soon developed a successful concern. This was further strengthened by the improvement of Mr. H. Y. Castner, an American chemist, who, in 1886, patented improvements for producing a more intimate mixture of the carbon with the caustic soda in a state of fusion by means of a carbide of iron, in this way cheapening by more than one-half the cost of manufacture of metallic sodium, which had been \$1 per pound. This concern was organized under the name of the Aluminum Company, Limited, and put up a large and expensive plant at Oldbury, near Birmingham, England. These works were started at the end of June, 1888, and they have been manufacturing up to within the past six or nine months. In common with the other manufacturers by the sodium process, they have been working at great disadvantage since the advent of the more successful electrolytic processes.

Early in 1888 the Alliance Aluminum Company started works at Wallsend-on-Tyne, England, using a process which was an innovation upon the Deville sodium process by using the fluoride or the double fluoride of aluminum and sodium, cryolite, as the compound to be reduced instead of the chloride or the double chloride of the metal. Professor Nette, the managing director of the concern, also had a process for reducing metallic sodium cheaply by allowing fused caustic soda to trickle over incandescent charcoal in a vertical retort. Some very excellent aluminum was produced at this works; they became involved in a lawsuit, however, with the Aluminum Company, Limited, and the newer processes coming up caused them also to close their works, which have now been shut down for over a year.

ALUMINUM PRODUCTION BY ELECTRICITY.

In spite of the broad claims of the Cowles Brothers to the use

of electricity for metallurgical purposes, the first actual reduction of aluminum in a metallic state on a practical scale by Deville in 1854 was, as we have seen, by the aid of electricity, electrically decomposing the chloride. Even then the idea was old, for Sir Humphrey Davy in 1810 publicly described the successful experiment made in 1807, in which he connected the negative pole of a battery of 1000 double plates with an iron wire which he heated to a white heat and then fused in contact with moistened alumina, the operation being performed in an atmosphere of hydrogen. The iron upon analysis was found to be alloyed with aluminum.

Bunsen in Germany and Deville in France, in 1854, each electrolyzed the double chloride of aluminum and sodium. Le Châtelier obtained English patent No. 1214 in 1861, and Monckton, in 1862, English patent No. 264 for the reduction of aluminum by aid of electricity. In fact, Richards says that the Monckton patent "proposes to pass an electric current through a reduction chamber, and in this way to raise the temperature to such a point that alumina will be reduced by the carbon present," showing that not only was the use of electricity for reducing aluminum old, but that the idea of the electric furnace was twenty years old at the date of the first of the Cowles patents in 1885.

Richards, in his work on aluminum, mentions and gives the published authority in each case of the processes for reducing aluminum with the aid of electricity; of Gaudin, 1869; Kagensbusch, 1872; Berthaut, 1879; and Gratzel, 1883.

The newer pure aluminum processes using electricity of Hall, Heroult, and the Bernard Brothers, with the help of Minet, together with the alloy processes of the Cowles Brothers and of Heroult, are the only ones that are now being worked upon a commercial scale, so far as I know, though perhaps the meritorious inventions of Mr. Grabau may have been reduced to practical working of late. Of this I am uncertain, or of what is being done by Herr Saarburger at Hemelingen, near Bremen. I only know that we no longer hear of the Aluminum & Magnesium Fabrik Company's aluminum in the competition of the markets, nor of any metal made by the sodium process.

Besides these, there have been a host of other electrical attempts and experiments for the manufacture during the past two years,

since the success of some of the other companies using electricity became known.

THE HALL PROCESS OF ALUMINUM PRODUCTION AND OTHER ELECTRIC PROCESSES.

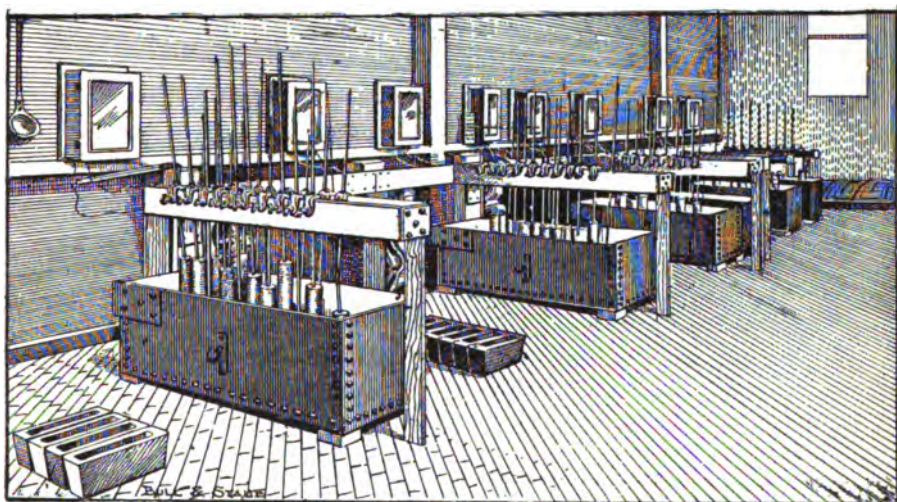
The Hall process of manufacturing aluminum is owned by the Pittsburgh Reduction Company, who have, in addition to 390 electrical horse power at work in Pittsburgh, another plant of about equal size at Patricroft, Lancashire, England, the Pittsburgh works commencing to manufacture in November, 1888, and the English works in July, 1890.

The Hall process consists in electrolyzing alumina dissolved in a fused mixture of fluorides of aluminum and sodium or of fluorides of aluminum and potassium, or, in fact, Mr. Hall has covered in his letters patent No. 400,667 a fused bath in which the alumina is dissolved in the fluoride of aluminum, together with the fluoride of *any* metal more electropositive than aluminum.

As the Pittsburgh Reduction Company uses the process, it places the mixture of fluoride salts in a row of carbon-lined iron tanks placed in series. The pots, together with their carbon linings and the reduced metal in the bottom of the pots, become the negative electrodes or cathodes. The positive electrodes or anodes are a series of 3-inch diameter carbon cylinders, attached by $\frac{3}{8}$ -inch copper rods to the copper conductors by the aid of suitable binding screw clamps. The current of 5000 amperes and 50 volts in one series, and of 2000 amperes and 20 volts in the other series, is turned on, and the mixture is melted by the heat caused by the resistance offered to the current by the fluoride mixture. In less than two hours' time the mixture becomes fluid, and alumina is added. The electrolyte then becomes a much better conductor, "the resistance of the pot" goes down to a normal one of about 8 volts, and the operation of electrolysis commences. The alumina in solution, or, as some claim, the fluoride of aluminum, is decomposed; the metal, being heavier than the electrolyte, sinks to the bottom of the pot, and the oxygen goes to the positive carbon electrode, uniting with a portion of the carbon and escaping as carbonic acid gas; or, as is maintained by some, the aluminum of the fluoride of aluminum is deposited, and the fluorine attacks the

dissolved oxide, reforming fluoride of aluminum, and thus maintaining the integrity of the original electrolyte bath, the oxygen going off, as in the other case, at the positive electrode.

While the actual fact as to which reaction takes place is not essential to the validity of the Hall patents, and the Pittsburgh Reduction Company makes no claims regarding the matter, it is our belief that the compound electrolyzed is alumina. I may say, in this connection, that this is the view of Professor J. W. Langley, Professor Richards, and of all the other metallurgists who



REDUCING POTS—PITTSBURGH REDUCTION COMPANY'S PROCESS.

have had experience with and have given the actual metallurgical operations careful study.

Among the reasons for our belief are the heat of formation of alumina, 391,600 calories; the fact that it requires only 2.8 volts to decompose it; the probable fact that the heat of formation of the aluminum fluoride is very considerable greater; the fact already established, that it requires a very much higher voltage than 2.8 to decompose the electrolyte that we use; and the fact, already mentioned, that when the bath gets out of alumina the resistance rises considerably (ordinarily about four volts), and that the heat rises rapidly in the pot until the electrolyte itself begins to de-

compose, and stifling white fumes of hydrofluoric acid begin to be given off.

Again, fluorine displaces oxygen in alumina; hence we reason that aluminum fluoride is a stronger compound than alumina. Sodium reduces aluminum fluoride—the basis of the Grabau process. Ergo, sodium fluoride is a stronger compound than aluminum fluoride. Hence, in a bath containing sodium fluoride, aluminum fluoride, and alumina, in nearly equal proportions, the order in which they will be decomposed by an electric current of graduated intensity, or in conditions similar to the Hall bath, will be alumina, aluminum fluoride, and sodium fluoride. Again, the electro-motive force required to decompose compounds is in proportion to the heat evolved in the formation of electro-chemical equivalent weights of the compounds; and sodium fluoride is thermally much greater than $\frac{1}{6}$ of a molecule of aluminum fluoride, or of a molecule of alumina.

According to my understanding of the case, the difference between the Hall process and the Heroult alloy process is this; Hall electrolyzes alumina made fluid at a lower temperature by dissolving it mechanically in a fused fluoride solvent, lighter than aluminum, which will not corrode the metal, and above all will not be itself decomposed by the electric current (or at least will not stay decomposed), and which is a sufficiently good conductor of electricity to allow the temperature of the molten bath not to reach much above the melting point of the metal. In the Heroult process they electrolyze alumina, made fluid by the intense heat of the electric arc, at a temperature at which the metal has to be protected by being alloyed with copper or iron in order to retain it.

DETAILS AND ADVANTAGES OF THE HALL PROCESS.

In the practice of the Hall process the heat is retained in the molten bath by a covering of finely powdered carbon on the surface of the molten mixture. On top of this carbon raft the powdered alumina is placed, and when the voltmeter attached to each pot shows a rising resistance, the pot-tender stirs in more heated ore from the surface of the pot. The carbon soon comes to the surface, when a fresh supply of ore is placed on it. The feeding is thus easily made continuous, and as the electrolyte remains

constant, it only requires tapping the metal off—or, as is rather crudely but very satisfactorily done, dipping the metal out in cast-iron ladles, and skimming the electrolyte back into the pots with the carbon rods—to make the entire operation continuous. The pots are run for months at a time. The following are the chief advantages of the continuity of the process :

1. *Purity of the Metal.*—After the first run of metal is cast, carrying with it all the iron and silica, or rather the reducible impurities of the electrolyte, the only other sources of impurity are in the pure alumina added and in the ash of the positive carbon electrodes, which are worn away in the proportion of a little less than weight of carbon to the weight of metal produced.

2. *Saving of Material.*—The loss of metal and ore in a finely divided state in the bath, which occurs when a shut-down is required, is avoided. To be sure, this loss can be largely avoided by re-melting again ; but in melting down the metal in a finely divided state it is found to be almost entirely re-dissolved. As continuously carried on, the loss of metal is practically nothing, every particle being reduced ; undoubtedly it is often reduced more than once by being re-dissolved before settling through the bath to the metal below, when the ore gets out of the electrolyte and it becomes acid. At the same time, as there is no slag or other waste product, solid or liquid, evolved, and as the gases can carry off none of the aluminum, all of the aluminum in the ore added is finally brought out in ingot metal, a result that is seldom experienced in the reduction of metals from their ores.

3. *Economy.*—The original heat of the electrolyte is constantly maintained, and the only supplies needed are the constant electric current, the alumina ore and fresh carbon electrodes to replace those worn out, with only occasional additions of fresh electrolyte to replace the small loss of that taken out with the ingot metal or that which has become decomposed by the workmen carelessly letting the pots get out of ore. This decomposition of the electrolyte means an infusible “cake,” as the workmen call it, settling to the bottom of the pot and filling it up. When the pots are not skillfully run, or more easily decomposing electrolyte mixtures are used, this accumulation shortens the run of the pot, and also decreases the output. In the regular practice of the Pittsburgh

Reduction Company there is practically no decomposition of the electrolyte, and a pound of aluminum is made with an expenditure of about twenty-two electrical horse power per hour.

This electrical energy expended in heat is not very expensive. Supposing water power to be used at a cost of \$12 per horse power per annum, allowing 25 per cent. for loss in converting mechanical into electrical energy, and supposing 75 per cent. of this energy to be converted into heat, Professor Richards has calculated the heat generated by one horse power during one year as 8,400,000 heat units.

The Hall process can be successfully carried on entirely independent of carbon, using a thick iron or copper tank, and either iron or copper electrodes. The deposition of the metal is nearly as large as with the use of carbon electrodes; but it is, of course, alloyed with copper or iron from the metal worn away from the positive electrode.

The Pittsburgh Reduction Company has made alloys of aluminum with iron and copper by this process similar in character to the alloys produced by the Cowles and Heroult alloy processes.

THE HEROULT AND MINET PROCESSES.

Almost at the same time that Hall invented his process for manufacture of aluminum, in the early part of 1886 (his first patent application dating July 9, 1886), M. Pierre Heroult commenced operations, and afterwards took out English patent No. 7426, of 1887, for fluxing alumina with cryolite. The bath was put into a graphite crucible, which served as a negative electrode, and this was put inside a larger crucible, the space between the two being filled with graphite, and the carbon positive electrode being immersed in the fused bath. The ideas of M. Heroult and Mr. Hall at the very start were very nearly identical. M. Heroult attempted to obtain an American patent, and was declared in interference with Hall; and, after the testimony as to dates of invention and of the application for patents, M. Heroult withdrew in favor of Mr. Hall. This process was practically abandoned for a while by M. Heroult in favor of his very successful alloy process of electrolyzing and reducing molten alumina; but since 1889, when a growing demand sprung up for pure aluminum, and the success

of the Hall process became known, I understand that two concerns have begun working under the same principles—the Aluminum Industrie Actien Gesellschaft, at Neuhausen, Switzerland, and a concern at Froges (Isère) in France, called the Société électro-métallurgique de France. I have seen some very pure and excellent metal from the Swiss concern.

The process commonly called “the Minet process,” as developed and used at the works of the Bernard Brothers at Creil, Oise, France, consists in electrolyzing a mixture of sodium chloride with aluminum fluoride, or with the double fluoride of sodium and aluminum, their English patent dating July 18, 1887, No. 10,057. This company, I understand, have been doing successful work, and are now putting on the market aluminum of good quality. Thus it will be seen that there have developed apparently three separate electrolytic processes for the manufacture of pure aluminum at about the same time, all of which are working on about the same lines. These, together with the already much-written-about Cowles and Heroult processes for the manufacture of aluminum alloys, have for the past two years distanced all competitors manufacturing by the aid of metallic sodium, and are to-day in the possession of the aluminum market of the world.

FUTURE PROCESSES OF ALUMINUM PRODUCTION.

And now I will close with a few remarks upon the prospects and possibilities of the future—a subject in which, as President of the Pittsburgh Reduction Company, I am both financially and technically very much interested.

First, let me preface what I have to say by stating that I am not at all afraid of any new processes of which the first we hear is the blast of trumpets and a general outcry through the newspapers of the very low cost at which the metal can be made, given in figures exact to a cent. I feel confident that either the inventor of such a process, or his friends, the company promoters, have so little sagacity and business sense that they will fail, even if they have a good thing; or else that they are simply attempting to further deceive the public and prospective investors with delusive prospects, which, if well founded, would have been the very

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reason for keeping the matter quiet until they had become organized, and secured their capital and protection, so far as possible, by letters patent. If an inventor has a meritorious process for the manufacture economically favorable to the processes now in vogue, the method would have to be so simple that he would be able easily to prove it, and then he would have no trouble in securing capital to help him. The first thing any sagacious capitalist would then do would be to insist that cost prices be kept quiet, at least until it should be proved on an actual manufacturing scale just what cost prices were. For very often a most delusive difference is found to exist between the theoretical cost price and actual cost price, as may be proved by the books of almost any well organized manufacturing concern.

THEORETICAL COST OF MANUFACTURE BY ELECTROLYSIS.

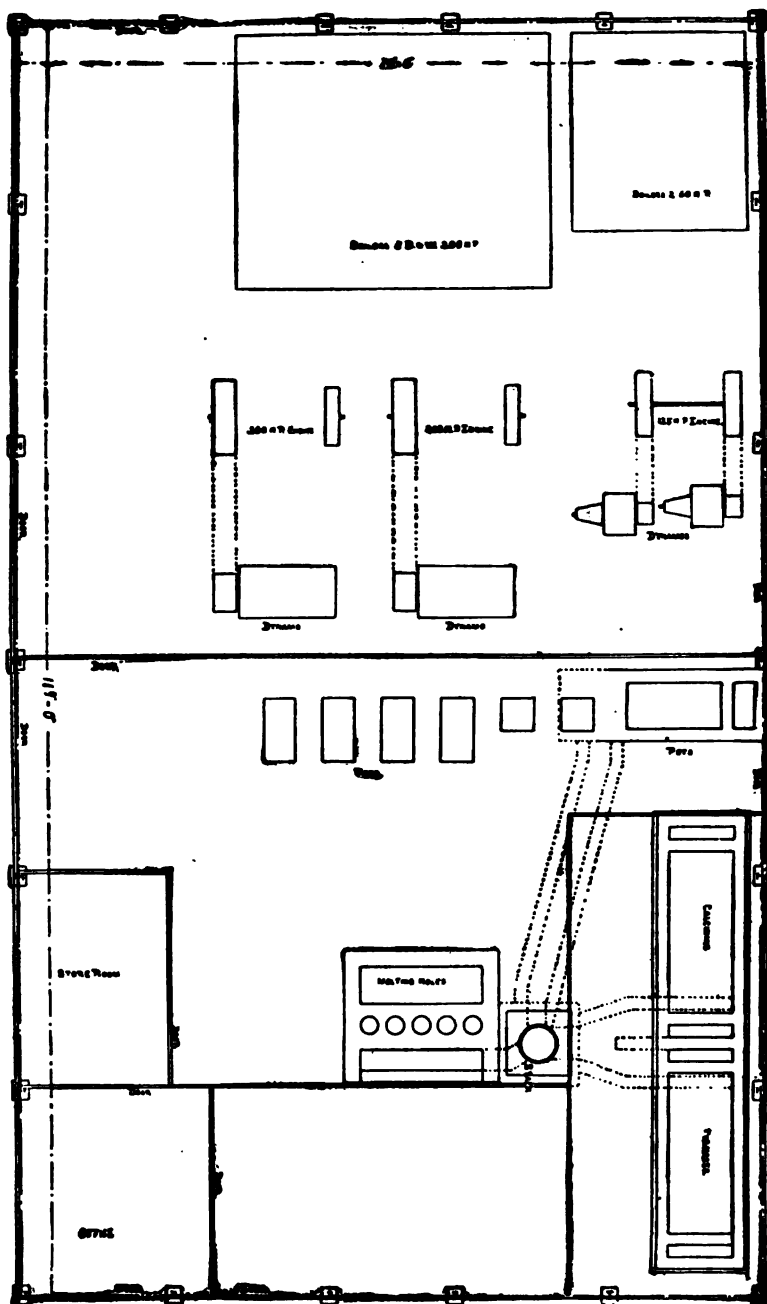
Theoretically, the cost price of the manufacture of aluminum by direct electrolysis has already been brought down very low as compared with the cost of the more complicated processes of a few years ago. The cost per pound is about as follows :

2 lbs. of alumina (Al_2O_3 , contains 52.94 per cent. Al_2) at 3 cts., \$.06
1 lb. of carbon electrode at 2 cts.02
Chemicals, carbon dust, and pots01
22 E. HP. exerted one hour, water power being used05
Labor and superintendence03
General expense, interest and repairs03
Total	\$.20

I would say here that while the actual cost of the metal produced by the Pittsburgh Reduction Company, or any other of the concerns mentioned as actually putting aluminum in limited quantities on the markets to-day, are nothing like these figures as a total, at the same time, as the most economical methods are used, figures approaching these will undoubtedly be attained ; and, moreover, improvements in new processes will in many cases probably be equally applicable in reducing costs by the present electrolytic methods. As stated before in this paper, no process can be devised that will give less loss of ore than that of the Hall process, where it is practically nil, nor is it probable that any other

method can be devised that is able to give purer metal than that made by the Hall process. Analyzing the items of cost given above, the ore will probably be the greatest item of expense in any successful process, and surely the oxide, alumina, is not only the richest and most easily prepared pure ore, but will prove one of the cheapest, if not the cheapest, of compounds from which to extract the metal. Quite surely no difference here in the art will make an insurmountable barrier of cost for the electrolytic processes now in use to compete against. The expenditure for other reagents than the ore, for carbon, and for chemicals, is now less than five cents per pound, with the Pittsburgh Reduction Company, and in the estimate can fairly be reduced to three cents per pound, for a large plant, with most favorable arrangements made for its supplies. In the item of electrical power there certainly may be room for a large curtailment of cost; but, even should this expenditure of electrical power be lessened one-half, or entirely done away with, heat alone being substituted as the energy for the reduction of the ore, it will be difficult to conceive of a method that would not require a cost of at least one cent for this heat, which would be a saving perhaps of four cents per pound upon this item of electrical power. However, I feel confident that should such processes be devised, the increased expenditure for chemicals and other reagents besides the amount quoted as necessary for the Hall electrolytic process will nearly, if not quite, counter-balance the saving in electrical energy expended in the Hall process.

In the items of labor, superintendence and general expense, interest and repairs, there may be material saving made by a process yielding metal more rapidly than by the comparatively slow electrolytic process. But the plant required by the Hall process is very simple—especially if located upon water power—and the repairs are very small in proportion to the output. It will be doubtful, therefore, if a saving of more than three cents per pound can be made, or one-half of the total estimated as necessary for the manufacture of aluminum by the Hall process. Thus the total saving probable, or, I think I am almost justified in saying, even in these days of wonderful invention, possible, is only about seven cents per pound over the cost of the Hall process. A greater



PLAN OF THE PITTSBURGH REDUCTION COMPANY'S WORKS.

saving than this may perhaps be made if some bright artist shall be able with Aladdin's lamp to rub the clay bank with his magic wand and extract "the silver from the clay" by his incantations; or, perhaps, more soberly, some one may find a method of reducing aluminum from some of its compounds as a by-product, the expense of which shall entirely or mainly be borne by the other valuable products made.

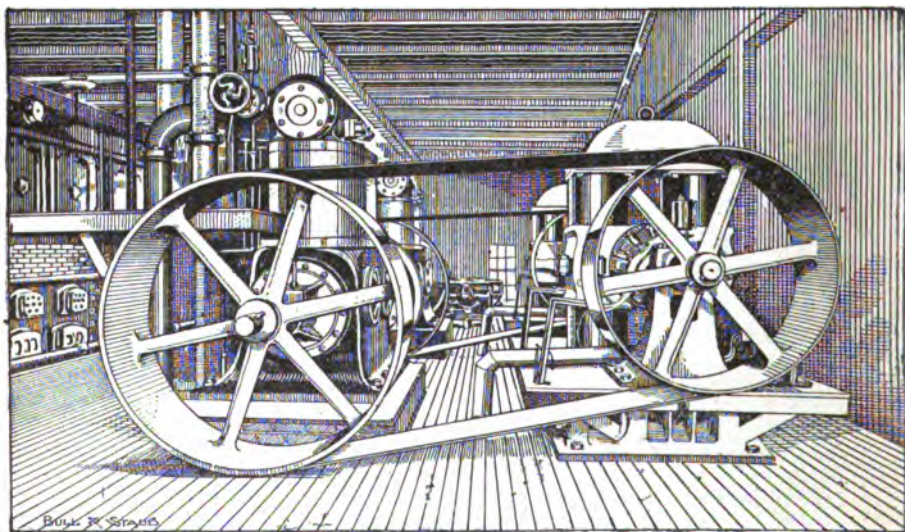
POSSIBLE COMPETITORS OF THE ELECTROLYTIC PROCESS.

In this connection, an ingenious method has been devised to electrolyze the sulphide of aluminum, or the double sulphide of aluminum and sodium, in a tank, closed and suitably insulated, and connected with a powerful electric current. The tank is filled with charcoal, covered with alumina, or, in case the double sulphide is to be made, with a mixture of alumina and some sodium salt. The tank is heated to incandescence by the electric current, and fumes of sulphur are forced into the tank. An atmosphere of bi-sulphide of carbon is produced; the excess is carried away by a condensing pipe, and is calculated to yield revenue enough to pay for the entire operation, which consists further in reducing the sulphide of aluminum produced by a portion of the bi-sulphide of carbon acting upon the alumina in the presence of the heated carbon. The sulphide of aluminum is electrolyzed in the lower part of the tank, the molten metal going to the bottom, where it is afterward tapped out. The evolved sulphur again attacks the hot coal and produces bi-sulphide of carbon. This process looks very pretty on paper, but, unfortunately, it has not thus far proved financially successful.

The only method which seems at all likely to supersede the electrolysis of alumina as the most economical method of manufacture of aluminum is some variation in the condition (such as performing under pressure or the like). The oxide, or an equivalent aluminum compound, would have to be cheaply prepared, by the aid of carbon at a much lower temperature than is now possible by the means already tried. If such a feat could be accomplished, the changed conditions under which the carbon was to work not being too expensive to attain, and the reduction being accom-

plished rapidly enough to admit of the process being used upon a large commercial scale, then the electrolytic methods of manufacturing aluminum would have to be relegated to the same fate that has already overtaken the sodium method of reduction. But, in the light of what I have already said, I venture here to predict a long life and a happy one yet for the electrolytic methods of manufacture of aluminum.

In closing, I wish to acknowledge my indebtedness to Professor Joseph W. Richards, of Lehigh University, not only for personal statements and suggestions, which I have embodied in this lecture, but also for data from his admirable book on aluminum. It is the first work on the subject printed in the English language, and I prophesy that it will always hold an authoritative position among the best treatises on the metallurgy and properties of aluminum, a place akin to that held by Percy's "Metallurgy of Iron and Steel."



DYNAMO ROOM — PITTSBURGH REDUCTION COMPANY.

DETECTION OF IMPURITIES IN ALCOHOL.

A great number of reactions have been indicated for the detection of impurities contained in alcohol. The action of sulphuric acid, bisulphate of rosanilin, of acetate of aniline, and of potassic permanganate are thought to give the best results.

Mixtures of alcohol were made containing $\frac{1}{1000}$ part of the substances usually found in alcohol or added thereto, and submitted to the action of the various reagents. A reagent which would not detect an impurity when present in the above quantity was rejected as unreliable. The results of the test follow :

Sulphuric Acid.—The quantity employed was 10 cc. acid to 10 cc. of the alcohol mixture. Above that quantity the alcohol becomes colored ; below it the sensibility of the test is greatly diminished. The table gives in degrees Savalle the intensity of the coloration obtained with the different solutions up to $\frac{1}{1000}$.

Products Dissolved in Alcohol.	Degrees Savalle Corresponding to Solutions Containing per Liter.			Limit of dilution distinctly marked by the color reaction.
	1 gm. intense black	.5 gm. black	225 gm. gray	
Furfural	9	3	$\frac{1}{2}$.01
Isobutyric aldehyde	8	4	$\frac{1}{2}$.125
Paraldehyde	7	2.5	$\frac{1}{2}$.125
Propionic aldehyde	5	2.5	trace	.250
Oenanthylic aldehyde	5	1	"	.250
Valerianic aldehyde	3	3	"	.125
Acetic aldehyde	2.5	trace	"	.500
Formic aldehyde	1.5	"	"	.500
Capryl alcohol	7	3	$\frac{1}{2}$.050
Isobutyl alcohol	6	2.5	$\frac{1}{2}$.125
Heptyl alcohol	4	trace	trace	.500
Amyl alcohol	2	"	"	.500
Acetate of amyl	3	"	"	.250

Bisulphite of Rosanilin.—The reagent should be made by the following formula :

$\frac{1}{1000}$ solution of fuchsin	20 cc.
Bisulphite of soda 34 degrees B	20 cc.
Sulphuric acid	3 cc.
Distilled water	200 cc.

It should be employed immediately after its preparation in the

proportion of 4 cc. to 10 cc. of the alcohol to be tested. The maximum intensity of coloration is obtained after a half hour's digestion.

The following quantities per liter of the substances named can be detected by this reagent :

Acetic aldehyde01 gm.
Oenanthylic aldehyde01 "
Oenanthylic acetate01 "
Valerianic aldehyde02 "
Propionic aldehyde05 "
Isobutyric aldehyde05 "
Paraformaldehyde50 "
Furfurol50 "
Butyric aldehyde50 "
Acetone50 "

The method cannot be used to determine the aldehydes quantitatively because the coloration is not proportional to the quantity of substance.

Acetate of Anilin.—The acetate of anilin in acid solution is the proper reagent for furfurol. It gives no reaction whatever with any of the substances mentioned above. The coloration developed is not greatly influenced by the relative proportion of the anilin and acetic acid. The quantity of anilin acetate in the reagent, however, should be fixed. Ten drops of anilin and 2 cc. of glacial acetic acid are the proper quantities to be used for 10 cc. of the alcohol under examination. The coloration is at its maximum after digestion for 30 minutes. The furfurol can be quantitatively determined. The reaction is excessively sensitive. A solution containing no more than 1 mg. furfurol per liter gives a distinct coloration, and it is possible to get a coloration with solutions containing no more than one millionth part of furfurol.

Permanganate of Potash.—When two or three drops of centinormal permanganate of potash solution are added to 10 cc. of pure alcohol, it requires about two minutes to obtain a complete reduction. When any of the impurities before mentioned, are added, the reduction is more or less rapid, but it is not possible to distinguish which of them is most reductive. In the presence of acids, however, the permanganate is reduced by three of them, and these are paraldehyde and isobutyric aldehyde and alcohol.

This reduction is found to be proportional to the quantity of aldehyde, but is independent of the concentration of the alcohol and of the degree of acidity.—*Ed. Mohler, Comptes Rendus*, 111, 187.

H. W. W.

BEES-WAX ADULTERATIONS.

The adulteration of bees-wax is usually performed with great skill, and is sometimes difficult to determine accurately, many complex compounds put out by the adulterators containing not the slightest trace of the article by the name of which it passes.

Most of the bodies used in adulterating, modify somewhat the characteristics of the wax. Thus, tallow, stearic acid, Japan wax, and Carnauba wax, cannot be added to bees-wax without altering its physical properties. Japan wax and stearic acid decrease the malleability and render it brittle; tallow makes it more soft and greasy; Carnauba wax elevates considerably the fusion point. Among other adulterants are, paraffins, fossil waxes, ozokerite, ceresine, fossil wax purified by treatment with sulphuric acid and distillation with water vapor, certain vegetable waxes, Chinese wax, wax, or waxy acids extracted from mutton suint, resin, and even mineral and organic powders. For analysis, the authors use the process given by Becker, Hehner and Hübl, which depends on the determination of the free and combined acids contained in the mixture. Bees-wax contains from 19 to 21 free acids and from 71 to 76 combined acids, under the form of ethers, calculated in milligrammes of KHO for 1 gm. of wax. From these two determinations, an approximate idea of what adulterant or adulterants have been used can be obtained. Thus, if the number representing the free and combined acids falls, respectively, under 19 and 71, some neutral product, paraffin, ceresine, etc., has been added. If the number representing the free acids is above 19, stearic acid has been added; if below 19, tallow has been added.

Besides these two determinations, the authors make three others: titration with iodine; determination of the alcohols and hydrocarbons contained in the sample. The authors, by different determinations, have fixed to the various adulterating matters numbers which represent quantitatively their composition; from these can

be determined in what sense they differ from bees-wax, and modify mixtures with it.

	Fusion Point.	Acids soluble in H ₂ O in mgr. of KHO for 1 gm. of product.	Free Acids in mgr. of KHO for 1 gm. of product.	Total Acids in mgr. of KHO for 1 gm. of product.	Fixed Iodine for 100 of product.	Vol. of H. at 0° and 760 mm. furnished by 1 gm. of product	Hydrocarbons for 100 of product.
	deg.					cc.	
Japan wax	47 to 54	2	18 to 28	216-222	6-7.55	69-71	0
Chinese wax . . .	53.5	2	22	218	6.85	72.3	0
Vegetable wax . .	47 to 54	2	17 to 19	218-220	6.6-8.2	73-74	0
Carnauba wax . .	83 to 84	0	4 to 6	79-82	7-9	73-76	1.6
Mineral waxes . .	60 to 80	0	0	0	0-0.6	0	100
Paraffins	38 to 74	0	0	0	1.7-3.1	0	100
Wax from suint .	62 to 66	0	95 to 115	102-119	13-18.5	0	14-18
Waxy acids of suint	50 to 62	0	155 to 185	159-189	2.6-2.8	0	0
Tallow	42 to 50.5	0	2.75 to 5	196-213	27-40	52-60	0
Stearic acid . . .	55.5	0	204	209	4	0	0
Resin	55.5	0	168	178	135.6	35	0
Yellow bees-wax .	62 to 64	0 to 1	19 to 21	91-97	8-11	53-57.5	12.5-14.5
White bees-wax .	63 to 64	0 to 2	20 to 23	93-110	2-7	53-57	11-13.5

A comparison of the numbers from the pure waxes given and those from the preceding shows that these substances will modify more or less the characteristics of the original body.

(1.) The fusion point of bees-wax is lowered if there are added to it the vegetable waxes of Japan, China, etc., certain kinds of paraffins, stearic acid or tallow. It is elevated if Carnauba wax and certain varieties of mineral waxes are added.

(2.) The free acids diminish with the addition of mineral wax, paraffin, tallow, and Carnauba wax. They increase with suint wax, waxy acids of suint, resin, and stearic acid. They vary little from the admitted limits with vegetable waxes, wax of China, Japan, etc.

(3.) The total acids diminish with the addition of mineral wax, paraffin, and a little with Carnauba wax. They increase rapidly with suint wax, and in a great proportion with the waxy acids of suint, resin, tallow, stearic acid and vegetable waxes.

(4.) The iodine titration diminishes with mineral wax, paraffins, waxy acids of suint, stearic acid, and in a small proportion with the vegetable waxes. It increases with the wax of suint,

tallow and resin. It remains within the limits with Carnauba wax.

(5.) The volume of H set free by potash diminishes with mineral waxes, paraffins, wax and waxy acids of suint, stearic acid and resin. It increases a little with vegetable waxes and Carnauba wax. It remains within the limits with tallow.

(6.) The hydrocarbons diminish in almost every case with the vegetable waxes, the waxy acids of suint, tallow, stearic acid, resin, and Carnauba wax. They increase only with the mineral waxes and the paraffins.

The authors go through the following steps in making an analysis of adulterated bees-wax.

(1.) The humidity is determined by drying at 100-110 degrees. The loss in weight should not exceed 1 per cent.

(2.) A weighed sample is treated with chloroform or essence of terebenthine, under heat, and filtered. The residue is composed of mineral or organic powders.

(3.) The fusion point and density. The density should be between 0.962 and 0.967.

(4.) About 20 gms. of the wax is treated with boiling water several times. This takes out any coloring matter, and from this the acidity can be obtained by titration with soda solution.

(5.) The product thus washed and dried is submitted to the following determinations :

(a.) The détermination of the free acids.

(b.) The determination of total acids.

(c.) The determination of acids not saturated, iodine titration.

(d.) The determination of the volume of hydrogen disengaged by the action of the potash.

(e.) The determination of the hydrocarbons.

—*MM. A. and P. Buisine (Bull. Soc. Chim. 5, 654-660).*

W. W. D.

ESTIMATION OF CAMPHOR FROM ITS ROTATORY POWER IN OIL SOLUTIONS.

Pure camphor was dissolved in the purest oils of commerce, and its specific rotatory power determined. The oils selected were olive, sweet almond, and huile de graines.

The several oils when saturated with camphor at 19 degrees contained of it the following quantities :

Huil d'olives	26.98 per cent.
" d'amandes	28.53 "
" d'graines	28.80 "

Correcting for the slight rotation of the oils, the specific rotatory power of the camphor was found to be as follows :

In huile d'olives—3 per cent. solution	(A) ₀ . 55° 42'
" " " 20 " " "	55° 12'
In huile d'amandes—3 per cent. solution	56° 47'
" " " 20 " " "	54° 19'
In huile de graines—3 per cent. solution	54° 24'
" " " 20 " " "	54° 7'

It is observed that the specific rotatory power (gyrodyn*) of camphor varies but little with the nature of the oil solvent, but increases with the dilution, thus conforming to the general rule.—*P. Chabot, Comptes Rendus 111, 231.* H. W. W.

THE MANUFACTURE OF LACTIC ACID AND ITS USE IN DYEING.

In 1887 Chas. N. Waite patented two methods for the production of lactic acid. The first (No. 365,655, dated June 28, 1887) consists in adding to a fermentable sugar in the presence of a neutralizer, such as carbonate of lime, a small proportion of glue and a lactic ferment. The temperature is to be kept at 105 degrees F. and the solution covered with petroleum to keep out air and foreign germs. In a subsequent patent (No. 368,032, dated Aug. 9, 1887 and assigned to the Avery Lactate Co. of Portsmouth, N. H.) Waite finds that ammonia will answer as a source of nitrogen provided air is excluded. The proportions preferred are 400 pounds water, 100 pounds white glucose, cane sugar or starch, 50 pounds carbonate of lime, $\frac{1}{2}$ pound sulphate of ammonia, $\frac{1}{4}$ ounce of phosphoric acid, and a small quantity of lactic ferment.

The following is taken from the patent specifications: "It is essential to the process that there should be an absolute exclu-

*It would be well to have some one word to express "specific rotatory power." I propose the word *gyrodyn* as both expressive and brief.—H. W. W.

sion of air, and hence I place the above mixture in a closed vessel having a small outlet, dipping under water, and remove whatever air there may remain in the vessel by a current of carbonic acid. This mixture I keep at a temperature between 40 and 50 degrees centigrade. Fermentation lasts from twelve to fifteen days, when all the sugar, starch, or glucose is transformed into lactic acid, which unites with the lime, forming the lactate."

"Among the advantages of my process I may name the following: First, the addition of a very small quantity of nitrogenous matter in its purest form—viz., ammonia—not more than enough to feed the lactic ferment, which appropriates it at once, thus preventing the simultaneous growth of other ferments; and, secondly, I avoid the addition of foreign matters not necessary to lactic fermentation, and which involve great difficulty in their subsequent removal from the lactate of lime at the end of the fermentation. My product is substantially free from foreign matter, is of a light color and an agreeable odor. As stated, I find it necessary to exclude every trace of air from the fermenting liquor. An artificial medium poor in nitrogen is not as favorable to the growth of lactic ferment as a natural medium (such as milk, decoction of meal, &c.) containing a large amount of nitrogenous matter. A vigorous ferment is not killed by a slight quantity of air, although its activity is greatly diminished, and hence milk, cornmeal, &c., may be fermented in open vessels; but I find that in order to make a lactic ferment live in an artificial medium every trace of air must first be removed."

According to Norton & Tuttle* the acid is now prepared in quantity by this process of proper quality for dyeing purposes and at such a price as to make it available. The samples which they used contained 43.5 per cent. lactic acid and were nearly colorless. The impurities present were sulphate of lime and a faint trace of iron. They have tried a series of experiments using lactic instead of tartaric, oxalic and acetic acids. The results may be summarized as follows:

Wool Dyeing.—With acid lactate and bichromate as mordant samples dyed with alizarine gave a deeper color than when tartar and bichromate was used. A comparison between oxalic acid and

*Technology Quarterly 3, 287.

bichromate, and lactic and bichromate, showed that the latter also gave a deeper shade with alizarine. When bichrome, alum and oxalic acid are used, the shade is also lighter than with bichrome, alum and lactic acid.

The results obtained by substituting acid lactate for tartar in mordanting with tin for alizarine were very striking. The color obtained with tartar was the well known reddish-orange, while the lactate shade was a very brilliant yellowish-red of great beauty, such as has hitherto been very difficult to produce upon wool with alizarine. It would appear that much more tin has been fixed in the case of the lactate with acid lactate and alum, and acid lactate and copperas, and it appears that the presence of lactic acid exercises a favorable effect upon the depth of shade produced by alizarin upon wool. The same thing is true of lactic acid and chrome alum. With logwood bark liquor, etc., upon wool, lactic acid gave results less favorable.

Cotton Dyeing.—It was found that the fixing power of the double lactate of antimony and potassa was not equal to that of tartar emetic.

Cotton Printing.—For cochineal pink the lactates give results very much superior to the tartrates. For use in white discharge on turkey red, lactic acid is fully equal to tartaric acid. In a general way the experiments of Norton & Tuttle show that the use of lactic acid is especially advantageous in alizarine dyeing on wood, and in cotton printing in place of tartaric and citric acids.

NEW PROCESS FOR THE DETERMINATION OF OXYGEN DISSOLVED IN WATER.

Following is the principle of the operation: The oxygen is absorbed by an alkaline solution of ferrous tartrate, added drop by drop to the water under examination, which has been colored with a little phenosafranine. As soon as the free oxygen has disappeared, the first drop of the ferrous salt added, provokes the decoloration of the liquid.

The author uses for the determination a flask of half liter capacity, having a glass cock on its bottom, into which is introduced about 400 cc. of mercury, 20 cc. of soda at 36 degrees Baumé, 20

cc. of a 20 per cent. ferrous tartrate solution, a drop or two of alcoholic solution of phenosafranine, and enough water to entirely fill the flask. A two-holed cork is then forced into the neck of the flask, taking care that no air is imprisoned beneath. Through one hole passes the neck of a Mohr's burette filled with a titrated solution of ferrous tartrate, and through the other a funnel-cock, which has been previously filled to the level of the cock, with some of the water under examination. Upon opening the cock in the flask, none of the mercury should escape, as the apparatus is a sort of truncated barometer which the atmospheric pressure keeps exactly filled. Sufficient ferrous tartrate to destroy the rose tint of the phenosafranine is then run in, while an equivalent quantity of mercury escapes at the bottom. 50 cc. of the water is then run in by the funnel-cock, the rose color reappearing under the influence of the dissolved oxygen; and then just enough ferrous tartrate is added again to destroy the color. Although the apparatus is exactly filled, it is very easy to shake the contents, as the reacting liquids rest upon the movable bottom of mercury. The oxygen can then be calculated from the amount of ferrous salt converted into ferric.

After one determination, the apparatus is ready for another, without changing its contents. It is always best to make three determinations in each analysis, and use the third as a base for calculation.—*M. G. Linossier, Bull. Soc. Chim.* 5, 63. W. W. D.

ANALYSIS OF A MIXTURE OF WAX, PARAFFINE, STEARINE, AND STEARIC ACID.

1. *Determination of Stearic Acid.*—Put in a flask 3 or 4 gms. of the mixture and bring it to a boil with 60 cc. of alcohol at 96 degrees; shake, cool, and titrate the solution with a half-normal alkali, using phenolphthaleine as an indicator. The proportion of stearic acid in the mixture can then be calculated from the number of cubic centimeters of half-normal alkali used in the titration, knowing that 7.8 cc. of the half-normal alkali equals 1 gm. of commercial stearic acid.

2. *Determination of Paraffine and Myricic Acid.*—Add to the flask containing the neutralized alcoholic solution 3 or 4 cc. of a

50 per cent. washing soda solution; attach to an inverted condenser and heat for an hour to saponify the material. When the saponification is finished, the excess of alcohol is distilled off, and the residue put in a dish, and mixed with some dry silica and short amianthus fiber. It is then dried at 100 degrees, pulverized, and treated under heat with either chloroform, ether or petroleum, which dissolves out the total paraffine and myricic acid representing a part of the wax.

To separate the myricic acid and paraffine, the chloroform, holding the mixture in solution, is distilled, then evaporated in a tared dish, dried at 100 degrees, and weighed. A part of this residue is weighed out and treated under an inverted condenser for an hour with 4 or 5 cc. of anhydrous acetic acid, which dissolves out the myricic acid. The liquid is then poured into a glass tube marked up to 10 cc., and divided into tenths. The dish is rinsed out with boiling acetic acid, and the whole is poured into the glass tube, which is placed in a water bath at 90 degrees. After remaining a while, it is corked and shaken strongly to emulsify the liquids, and then replaced in the bath. When the acetic acid has become clear, the volume of undissolved matter floating upon the acid is read off. This operation of agitation and replacement in the water bath is repeated until a constant volume of undissolved paraffine is obtained, from which the weight can be calculated, knowing that 1 gm. of paraffine equals 1 cc. By subtracting the weight of the paraffine from the weight of the residue dissolved in chloroform, the weight of the myricic acid is obtained.

3. *Determination of Stearine.*—The saponified matter insoluble in chloroform is dissolved in boiling water, filtered to separate the silica and amianthus, and the filtrate treated with a large excess of dilute nitric acid to set free the fatty acids, filtered again, and titrated for glycerine, after neutralization and precipitation by acetate of lead, with bichromate of potash. From the weight of glycerine the weight of the stearine or fat can be calculated, knowing that 5 gms. of anhydrous glycerin equal 95 gms. of stearine.

These are determined by this method:

1. Stearic acid by alkalimetric titration.

2. Paraffine by measuring the part insoluble in acetic acid.
 3. A part of the wax, myricic acid, by subtracting the weight of the paraffine from the weight of the residue soluble in chloroform.
 4. Stearine by titration of the glycerin.
 5. The second part of the wax, cerotic acid, by difference.
- M. Ferdinand Jean, Bull. Soc. Chim.* 5, 3. W. W. D.

NEW BOOKS.

Richter's Organic Chemistry.*—It is not saying too much of this book to call it one of the best laboratory hand-books upon the subject ever written. The successive editions have been improved in every case and made more complete and convenient. In late editions the author has followed a plan greatly to be commended in introducing references to original papers, so that the student can follow up statements conveniently and attain full knowledge. In this edition a chapter is given upon "The Tautomeric Theory"; the chapter upon the Determination of Molecular Formulae has been enlarged; a chapter entitled "Recent Views Relating the Theory of Structure" has been added; the section upon the carbohydrates has been entirely rewritten, etc. In all some 300 pages have been added to this second American Edition. The translation seems to be well done. Spacial is spelled "spatial" in several places, (pp. 49, 50, 63) and the translator speaks of a radical as univalent on page 45 and as monovalent on page 50. E. H.

Muter's Manual of Analytical Chemistry.†—This book is written from the standpoint of the pharmacist. It contains, 1st, a chapter on "The Processes Employed by Practical Chemists." The author apparently does not understand the distinction between fluid and liquid since he employs the former term on pages

*Chemistry of the Carbon Compounds or Organic Chemistry. By Prof. Victor von Richter, University of Breslau, authorized translation by Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Second American, from the sixth German Edition, 12mo. pp. XVI, 1040. With Illustrations. Phila.: P. Blakiston, Son & Co.

†A short Manual of Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic. Arranged on the principle of the course of instruction given at the South London School of Pharmacy. By John Muter. First American from the Fourth English Edition. Edited by Claude C. Hamilton, 8 vo., pp. XII, 205.

1 and 6 where the latter is meant. Under the section on fusion we learn that "a peculiar kind of fusion, called cupellation, is resorted to in the assay of gold and silver," which is certainly a novel way of putting it.

Chapter II treats of the detection of the metals and gives the usual tests under each metal. Chapter III treats of the Detection and separation of acidulous radicals. We can imagine what is meant by "Acidulous Radical," but do not know. It is evident from the methods given that the author is not familiar with either of the modern methods for detecting the haloids in mixtures containing two or more of them. Chapter IV treats of Qualitative Analysis as applied to the Detection of Unknown Salts and contains tests for some organic compounds, such as acetanilide, chloral hydrate, chloroform, saccharine (which the author calls glusidum) not found in the ordinary text-book; chapter V treats of the Qualitative Detection of Alkaloids and Poisons, Chapter VI, Weighing, Measuring and Specific Gravity, Chapter VII of Volumetric Quantitative Analysis; Chapter VIII of Gravimetric Quantitative Analysis of Metals and Acids, Chapter IX of Ultimate Organic Analysis, Chapter X of the Analysis of Water, Air and Food, Chapter XI of the Analysis of Drugs, Urine and Urinary Calculi, and Chapter XII of the Analysis of Gases, Polarization and Spectrum Analysis. The book contains a good deal of information in small compass and will no doubt prove useful. The paper and printing are fair; the cuts are poor and in some cases miserable.

E. H.

Barker's Chemistry.*—This is a new edition of a well known book and is noteworthy for its short, clear, pithy sentences. With all due deference to Prof. Barker, however, we believe he has not treated his subject in the best order. We find, first 95 pages upon Theoretical Chemistry; and while this may be *good* for a beginner it will certainly be neither easy nor pleasant. For a similar reason the periodic system seems to us not the best arrangement for an elementary text-book. In other respects the book is an excellent one.

E. H.

*A Text-Book of Elementary Chemistry, Theoretical and Inorganic. By George F. Barker, M. D. Professor of Physics in the University of Pennsylvania, Second Edition, Revised and Enlarged. 12 mo., pp. IX, 348. Louisville, Ky.: John F. Morton and Co.

THE

Journal of Analytical AND Applied Chemistry.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
WORCESTER POLYTECHNIC INSTITUTE.]

GEORGIA MARBLE.

BY LEONARD P. KINNICUTT AND FREDK. A. BIGELOW.

During the past five years a large amount of Georgia marble has been brought into the northern market. The deposits from which this stone is taken are situated at Tate, a small village about 50 miles north of Atlanta, and cover an area of about 7000 acres.

The marble occurs very near the surface, varying from one or two inches to three feet. It is characterized by its very coarse crystalline structure and its extreme whiteness, although mottled black, and pink varieties are also found in the same locality. These deposits have been worked more or less for fifty years, but it was not until 1885, when railroad facilities were obtained, that the marble obtained notoriety as a building stone.

An analysis of this marble gave the following result :

Specific Gravity	2.723	
Calcium Carbonate	98.96	per cent.
Magnesium Carbonate	0.13	"
Alumina	0.22	"
Iron Oxide	None	"
Silica	0.61	"
	<hr/> 99.82	
Absorption of water, specimen dried at 110° C. .	0.0401	per cent.
Loss in weight, by being exposed for one week to an atmosphere saturated with moisture and carbon dioxide	0.0832	"
Loss in weight, by being exposed for one week to an atmosphere saturated with moisture and sulphur dioxide	0.2406	"

A very fine grained calcium carbonate marble, containing 98.66 per cent. of calcium carbonate, and a fine grained dolomite marble, containing 43.20 per cent. calcium carbonate and 53.68 per cent. magnesium carbonate, gave by the last three tests the following results :

	Calcium Carbonate Marble.	Dolomite Marble.
Absorption of water	0.0614 per cent.	0.0477 per cent.
Loss by action of carbon dioxide .	0.0318 "	0.0196 "
Loss by action of sulphur dioxide	0.1786 "	0.0640 "

These tests indicate that the Georgia marble absorbs less water than either the fine grained carbonate or the dolomite marble, while the loss in weight by the action of both carbon dioxide and sulphur dioxide is greater. The surfaces of the Georgia marble, however, after the action of the above gases, were perfectly smooth, its edges remaining sharply cut, while the surfaces of both the other marbles, and especially the dolomite marble, were sandy and gritty, and the edges had a tendency to crumble.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
WORCESTER POLYTECHNIC INSTITUTE.]

FIRE-CLAY FROM MT. SAVAGE, ALLEGANY COUNTY, MARYLAND.

BY LEONARD P. KINNICUTT AND JOHN F. ROGERS.

The clay from which the well known Mt. Savage fire-brick is made is found as a very hard rock-like mass, only to be obtained by blasting, in veins 7 to 14 feet in thickness, which appear to belong to the carboniferous period. As first taken from the mine, it is in the form of large blocks of a rich gray or a dark brown color, with highly polished surfaces, which are often beautifully mottled. After exposure to the air for three or four months, these blocks can be easily broken, by aid of a sledge hammer, into small ones which still have highly polished surfaces. The clay is almost infusible before the blow-pipe, and on this account, as well as on account of its peculiar formation and structure, a full and complete analysis is not devoid of interest.

It has a sp. gr. of 2.54 and a hardness of 3.5. An ultimate analysis gave the following result :

Water	9.88 per cent.
Silica	60.19 "
Alumina	29.10 "
Iron Oxide	0.89 "
Lime	None
Magnesia	Trace
Alkalies	0.03 "
Carbon	0.02 "
Total	100.10 "

This analysis shows that the clay is free from any admixtures of feldspar or other double silicate, and only contains 0.92 per cent. of fluxing substances. The value of a fire-clay, however, depends not only on the absence of double silicates and fluxing substances, but also as Bischof has shown, on how much of the silica exists united to the aluminum and how much in the free state as sand.

The determination of the free and combined silica was made according to the method proposed by Forchhammer, and gave the following results :

Combined silica	28.09 per cent.
Free silica or sand	31.84 "
Hydrated silica	0.23 "

Uniting these results with the results obtained by the ultimate analysis, we have as the composition of the clay :

Combined silica	28.09 per cent.
Sand	31.84 "
Hydrated silica	0.23 "
Alumina	29.10 "
Iron oxide	0.89 "
Alkalies	0.03 "
Carbon	0.02 "
Water	9.88 "
Total	100.08 "

Allowing, as Brongniart and Malaguti do*, that the combined silica, alumina and water are united chemically, we have for the percentage composition of the kaolin that occurs in this clay—

Silica	42.08 per cent.
Alumina	43.22 "
Water	14.70 "

*J. pr. Chem. 31, 121.

These amounts are very nearly those that would be required by a kaolin having the formula, $2\text{Al}_2\text{O}_3, 3\text{SiO}_2, 4\text{H}_2\text{O}$, and the composition of Mt. Savage clay can be considered as—

Free sand, or silica . . .	SiO_2	31.84 per cent.
Kaolin	$2\text{Al}_2\text{O}_3, 3\text{SiO}_2, 4\text{H}_2\text{O}$	67.07 “
Iron oxide	FeO	0.89 “

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
WORCESTER POLYTECHNIC INSTITUTE.]

PURIFICATION OF THE SEWAGE OF WORCESTER, MASS., BY CHEMICAL PRECIPITATION.

BY LEONARD P. KINNICUTT AND HARRISON P. EDDY.

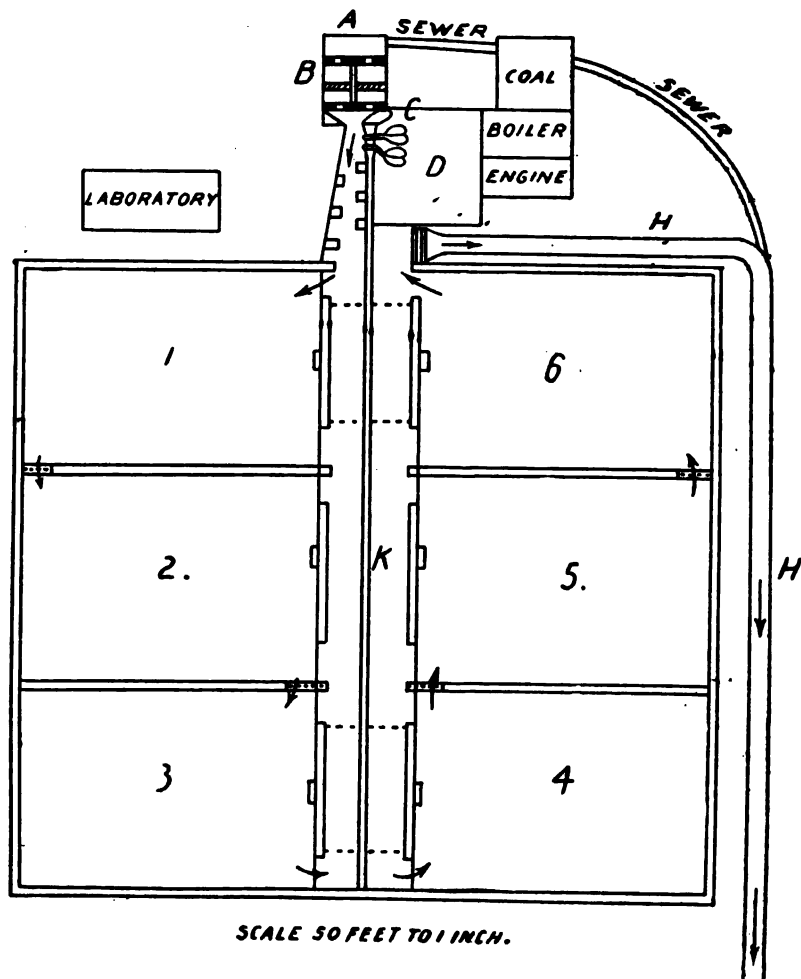
The only large plant in the United States for the purification of sewage by chemical precipitation is at Worcester, Mass. A brief description of this plant, together with the analysis of the sewage, effluent and sludge, may therefore be of interest.

The sewage of Worcester contains notably large quantities of the waste products of various manufacturing processes, and unusually large amounts of free acid and iron salts. The sewage, however, receives not only all the surface drainage of the City, but also part of the flow of a small manufacturing stream, so that the daily flow is very large, being in dry weather about 12,000,000 gallons per day. The following analysis, being the mean of a large number, gives the average composition of the sewage :

Analysis of sewage. Parts in 100,000.

Total solids	57.36
Volatile solids	14.01
Fixed solids	43.35
Suspended solids	16.83
Volatile solids	5.51
Fixed solids	11.32
Soluble solids	40.53
Volatile solids	8.50
Fixed solids	32.03
Chlorine	4.02
Free ammonia	1.451
Albuminoid ammonia	0.502
Sulphur trioxide	4.10
Ferrous oxide	7.50
Acidity in terms of H_2SO_4	3.80

Although the average acidity of the sewage does not run very high, yet at certain hours of the day, it is equal to 120 parts H_2SO_4 , or 70 grains to a U. S. gallon. The method now in use for the purification of the sewage is the one known as the Coventry process. Lime is added until the sewage is just alkaline, and then crude sulphate of aluminum; although the amount of ferrous sulphate in the sewage is often so large that the addition of the sulphate of aluminum is unnecessary.



The works consist of a boiler and engine house, a mixing-room for the chemicals, precipitation tanks, sludge well, etc., so arranged that their capacity can be easily doubled.

Reference to the drawing may make the arrangement more easily understood.

The sewage is brought by the outfall sewer *A* to the gate-house *B*, which is divided into two parts, each part containing an iron screen. The gross matters in the sewage are thus removed, and by means of gates the sewage can be carried through either part, allowing a continuous flow while the screens are being cleaned. From the gate-house the sewage runs through the channel *C* to the tanks. From this channel, by means of a small pipe, a little of the sewage is carried into the mixing-room *D*, where there are four mixing tanks, two for the lime and two for the alum. The mixing and dissolving of the chemicals is aided by mechanical stirrers run by steam, and the lime and alum, which after this treatment are partly in suspension, partly in solution, are carried back by pipes into the channel *C*. This channel is furnished with baffle plates made of wood, and the fall being about one foot, the chemicals become thoroughly mixed with the sewage.

The sewage then enters the precipitating tanks; these are six in number, made of brick, with concrete floors one foot in thickness. They are each 66 feet long, 100 feet wide, and 6 feet in depth,—the total capacity being 1,500,000 gallons. They are so arranged that they can be used intermittently or continuously, and for the purpose of removing the sludge and cleaning the tanks, any one can be shut off from all the others.

The sewage enters the tank marked 1, and from there flows to 2, 3, 4, 5, 6, the flow, however, being so slow that on looking at the tanks when filled, very little movement of the water is noticed. The time required for any given volume of water to pass through the six tanks is about four hours, thus allowing full time for complete precipitation.

The clear effluent passes over a weir at the end of tank 6, and falls over stone steps into the effluent channel *H*, which conducts it to the Blackstone River. Provision is also made, however, for removing the clear effluent from any one of the tanks. The concrete bottom of each tank inclines to the centre, where there is an open drain; these drains are connected with the sludge-pipe *K*,

which carries the sludge to the sludge-well *L*. Here the sludge is raised fifteen to twenty feet by means of a pump, and is conducted by a pipe to a sandy plot of land having an area of about fifteen acres.

Concerning the chemicals, the lime is ground up and the powder carried by a bucket elevator to the top floor, where it is sifted, and the coarse parts returned to the grinders to be again crushed.

The sulphate of aluminum is bought in the form of a fine powder.

These chemicals are run through hoppers into the agitators, and there thoroughly mixed with a little crude sewage taken from a point just below the gate house, and lifted by means of a centrifugal pump to the top of the agitators.* From the agitators the mixture is carried into the main body of the sewage, at the head of the sewage channel. There are two sets of two agitators, one for the lime, one for the aluminum sulphate. They are upright wooden vats, of 1600 gallons capacity, containing revolving arms driven by machinery.

The sewage, as it now comes to the works, varies greatly from hour to hour, sometimes containing large amounts of acid liquors and iron salts, and at other times being nearly neutral, containing very little mineral matter. Tests are made during the day and night to determine roughly the amount of acid present, and from these tests the amount of lime and sulphate of aluminum to be used is determined. At times it is necessary to add 150 grains of lime to a gallon of sewage. At other times the amount is reduced to two or three grains. On the average about one ton of lime is used for 150,000 gallons. The amount of sulphate of aluminum also varies greatly, depending upon the amount of iron-salts present in the sewage. The average amount does not exceed 100 lbs. per 100,000 gallons of sewage.

The greatest amount of precipitation takes place in the first precipitating basins. The first and second basins are cleaned every thirty hours, the third every two to two-and-a-half days, the sixth once a week. The sludge, which at present contains over 98 per cent. of water, is carried from the sludge well by a pipe line to the

*We had advised the use of thoroughly slaked lime, and its addition to the sewage in the form of milk of lime; but it is only since this article was written that this has been put in practice. The amount of lime thus saved is about one-third of a ton for each 150,000 gallons.

sludge fields, a sandy plot of about fifteen acres. The water gradually sinks into the sand, and at the end of eight days the sludge contains only 85 per cent. of water, and can be shoveled, and otherwise handled.

The effluent that is obtained by the use of the above chemicals, is free from odor, has only a slightly alkaline or limy taste, and as a rule contains only a very small amount of suspended matter. When placed in stoppered bottles, it remains clear and develops no odor.

The following analysis, being the mean of a large number, shows the average composition of the effluent.

Analysis of effluent. Parts in 100.000

Total solids	46.36
Volatile solids	5.85
Fixed solids	40.41
Suspended solids	1.97
Volatile solids	0.98
Fixed solids	0.99
Soluble solids	45.29
Volatile solids	4.87
Fixed solids	39.42
Chlorine	3.22
Free ammonia	1.168
Albuminoid ammonia	0.338
Sulphur trioxide	3.10
Ferrous oxide	0.20

The effluent is far from being pure water, but the amount of organic matter that it still contains, would, I believe, cause no nuisance even when run into a stream whose volume was only ten times its own.

The sludge as it arrives at the sludge beds is a thin pasty mass, containing, as I have said, about 98 per cent. of water. There are at the present time, 24 sludge beds, rectangular in shape and about 100 feet square. One day's sludge, about 75,000 gallons, is pumped upon two of these beds, and eleven days are allowed to intervene before any more sludge is placed on these particular beds. At the end of this time, the sludge contains about 85 per cent. of water, has the consistency of thick paste, and can be easily handled. The beds are situated in low sandy ground, and have been in constant use for more than a year, and no disagreeable odor has as yet been noticed. This method for disposing of the sludge will be continued until the entire area has been graded, after which

the sludge will be burned. That this can easily be done, is shown by the fact, that after the sludge has remained on the fields for a month, it contains 35 per cent. of solid matter, and if heaped up in piles and ignited, the organic matter can be completely burned out, or a whole bed in situ can be burnt by igniting the surface in a number of places with hot ashes. A complete and careful analysis of the sludge has been made, which has given the following results :

ANALYSIS OF SLUDGE.

Sludge as it comes from the sludge-well.

Water	98.78 per cent.
Total solids	1.22 "
Volatile solids	0.514 "
Fixed solids	0.706 "

Sludge after being exposed on the sludge-fields for ten days.

Water	84.21 per cent.
Total solids	15.79 "
Volatile solids	6.10 "
Fixed solids	9.69 "

Sludge after being dried at 110 degrees C.

Ash	66.01
Carbon by combustion	9.44
Hydrogen by "	1.87
Nitrogen by "	12.55
Oxygen, etc.	10.13
	<hr/>
	100.00

ANALYSIS OF ASH OF SEWAGE SLUDGE.

Silicon oxide, SiO_2	15.26 per cent.
Sulphur trioxide, SO_3	1.30 "
Phosphorus pentoxide, P_2O_5	4.06 "
Carbon dioxide, CO_2	0.96 "
Chlorine, Cl	2.17 "
Ferric oxide, Fe_2O_3	53.58 "
Aluminum oxide, Al_2O_3	4.99 "
Calcium oxide, CaO	16.01 "
Magnesium oxide, MgO	Trace
Copper oxide, CuO	0.15 "
Sodium oxide, Na_2O	1.40 "
Potassium oxide, K_2O	Trace
	<hr/>
	99.89

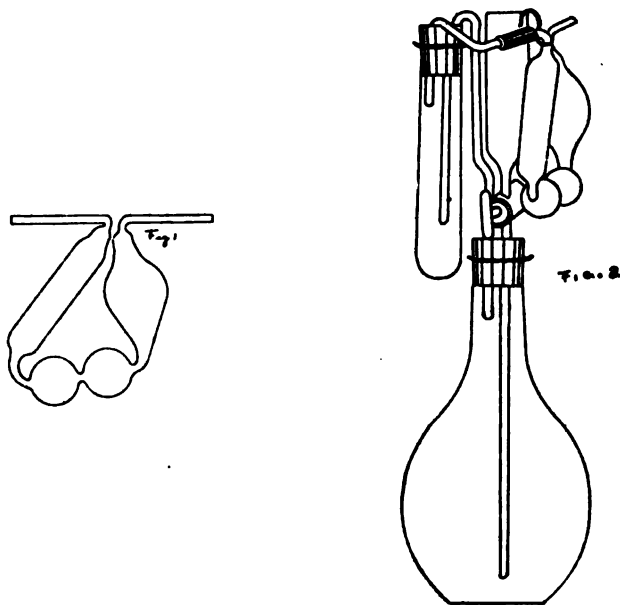
In the moist sludge, the calcium and iron are, to a large extent, in the form of hydrates, and the presence of calcium hydrate prevents disagreeable odors from being perceived at the sludge beds.

The theoretical manurial value of the sludge after remaining ten days on the fields, is from \$8 to \$10 per ton; when dried at 110° C., \$40 to \$50. Unfortunately, the theoretical and practical value of sewage sludge are by no means the same, and we believe that very little market will ever be found for the above material. Whether an ash having the composition shown by the above analyses has any value remains to be determined.

A NEW ABSORPTION BULB.

BY G. L. NORRIS, PENCYD, PA.

The bulb, shown $\frac{1}{4}$ size in Fig. 1, was designed especially for use in the determination of sulphur in iron and steel by the Eliot, or iodine method. It is also well adapted for use with



permanganate of potassium in Dr. Drown's method for sulphur. It is compact, readily filled, emptied, and washed out. When set up as shown in Fig. 2, it makes a very compact and convenient piece of apparatus, that may be used on the hot plate, doing away with a lamp-stand.

TREATMENT OF ZIRCONS IN PREPARING PURE ZIRCONIUM CHLORIDES.

BY F. P. VENABLE.

Linnemann (Sitz. Ber. Kais. Akad. d. Wissenschaft, vol. II, 1885, translated in London Chemical News LII, 233 and 240) has published an account of the "Treatment and Qualitative Composition of Zircon." All previous methods of breaking up the zircon and purifying the zirconia have presented numerous difficulties and proved decidedly unsatisfactory.

Having occasion to prepare some of the compounds of zirconium in considerable quantity and of chemical purity, I adopted the methods of Linnemann. In the course of my work, I have found it advisable to modify the process in several respects, and I make this publication in order that my experience may be available, and perhaps serviceable, to others.

In the first place, I have found the mechanical preparation can be simplified. I have used North Carolina zircons, and have found it sufficient to pulverize them roughly in an iron mortar and then grind in an agate mortar until the powder passed through a 100-mesh sieve. The preliminary exposure during ten days to vapor of hydrofluoric acid and the grinding until the powder passed a silk sieve seemed both unnecessary. The fine powder was repeatedly boiled with strong hydrochloric acid and washed with water. 500 gms. treated in this way lost 17 gms., the hydrochloric acid thus dissolving 3.40 per cent. of the whole. The fusions were made in nickel crucibles, which are very much cheaper and less attacked than the silver recommended by Linnemann. The loss comes chiefly in the cracking of the crucibles during the cooling after fusion. The crucibles used held a charge of 100 gms. zircon, 400 gms. sodium hydroxide, and 20 gms. sodium fluoride. This is one-half the amount of sodium fluoride recommended by Linnemann, but proved sufficient.

The sodium fluoride should be dried beforehand. The sodium hydroxide is first thoroughly melted and the fluoride then added. The mass should be brought to a fairly high temperature and then the zircon powder added. A rapid evolution of gas follows the introduction of the powder. The mass should be well stirred by means of a nickel stirrer—a narrow strip of sheet nickel fastened to

a glass rod answers the purpose and keeps the hands beyond the reach of hot alkali occasionally thrown out. If the bubbles threaten to rise over the edge, temporary removal of the lamp secures their subsidence. The crucible should not be allowed to cool too far, however. Much seems to depend upon carrying through the reaction rapidly at a high temperature. I have at times doubled and even tripled the length of fusion at a lower temperature without securing the thorough breaking up of the zircons obtained at a high temperature. After the first violent boiling, a quieter period follows. The end of the reaction is shown by a thickening of the mass and the rising of large bubbles here and there; also sometimes by a fine spitting or spray. In several instances where weights were kept the undissolved or unattacked portion of the zircon powder amounted to less than .5 per cent.

The melted mass was poured out upon pieces of sheet nickel for cooling. After solidifying enough to handle with tongs, it was broken off and plunged in a beaker of cold water. Water was also put in the crucible, after it had cooled, to dissolve off the portions adhering to the sides.

The water separates the sodium silicate from sodium zirconate, leaving the latter undissolved. The separation by means of water is far from perfect, some of the zirconate going into solution, though not enough usually to make it worth while to attempt to regain it. The sodium zirconate is dissolved in dilute hydrochloric acid and evaporated several times to dryness with fresh amounts of acid in order to drive off the hydrofluoric acid. There is a good deal of silica left with the undissolved portion. This is separated after evaporation to dryness. The dried mass is leached with dilute hydrochloric acid. There is difficulty sometimes in extracting all of the zirconium chloride in this way. Of course the solution contains large quantities of salt besides other substances. Zirconium hydroxide is precipitated from these by ammonium hydroxide and then thoroughly washed in large jars by decantation. The crude zirconium hydroxide is next dissolved in strong hot hydrochloric acid, using as small an amount as possible. This solution is evaporated to dryness and the crude zirconium chloride obtained placed in a large funnel and washed with a mixture of strong hydrochloric acid and four parts of alcohol. This mixture is poured

upon the mass in the funnel and allowed slowly to drain through. Some zirconium chloride is dissolved, but can be recovered by evaporation. The mass in the funnel is left white, and fairly pure.

To complete the purification, this mass is taken and repeatedly crystallized from boiling hydrochloric acid, until the acid gives no test for iron, which seems the most persistent among the impurities. I have commonly found it well to repeat this crystallization more than twenty times. The pure oxychloride is obtained in well-formed crystals of glistening whiteness. This method of crystallizing from hydrochloric acid used by Linnemann is the only satisfactory one for purifying the zirconium chloride. I have tried the precipitation by hydrogen dioxide as recommended by Bailey, but the consumption of pure dioxide is very large, and a heavy source of expense, and the pentoxide or mixed oxides yielded is not nearly so convenient as the chloride for further working with.

The method described above is shorter than the tedious and expensive treatment with hydrochloric acid, alcohol and ether. Judging from an attempt at carrying it out on a small scale, the amount of ether required in purifying the product from a kilo of zircons would be very large indeed.

The modifications in the process have throughout the aim of cheapening and shortening Linnemann's process, and were successful in both directions, at least under the conditions under which I worked.

A qualitative analysis of the different products obtained while thus decomposing the zircon was made under my directions by Mr. John M. Morehead. It differed in several noteworthy particulars from that made by Linnemann.

In the first place, the hydrochloric acid used in the preliminary treatment of the zircon powder extracted a large part of the total tin present. Linnemann does not mention tin as occurring in this solution. No lithium was discovered in any of the solutions, nor any bismuth and zinc. The list of elements found by Mr. Morehead is, therefore, shorter than Linnemann's, who reports sixteen. The list found was sodium, potassium, magnesium, calcium, aluminium, iron, lead, tin, uranium, erbium, silicon and zirconium. Undoubtedly, a large portion of these come from foreign matter mixed with the zircons and sifted into the cracks in

the crystals so as not to admit of separation. A number of the rare elements were looked for without avail. No thorough spectroscopic examination was made, however.

Mr. Morehead also made several quantitative determinations of the iron, silicon and zirconium, resulting as follows :

Per cent.	Zirconium Dioxide,	62.82	62.59	63.12	62.80
"	Silica,	34.10	34.20	33.52	34.10
"	Ferric Oxide		3.29		

or, taking the means,

$$\begin{array}{rcl}
 \text{ZrO}_2 & = & 62.83 \\
 \text{SiO}_2 & = & 33.98 \\
 \text{Fe}_2\text{O}_3 & = & 3.29 \\
 \hline
 & & 100.10
 \end{array}$$

It is not right to calculate the iron as all in the oxidized condition, as much of it comes from the iron mortar, and can be easily separated with a magnet.

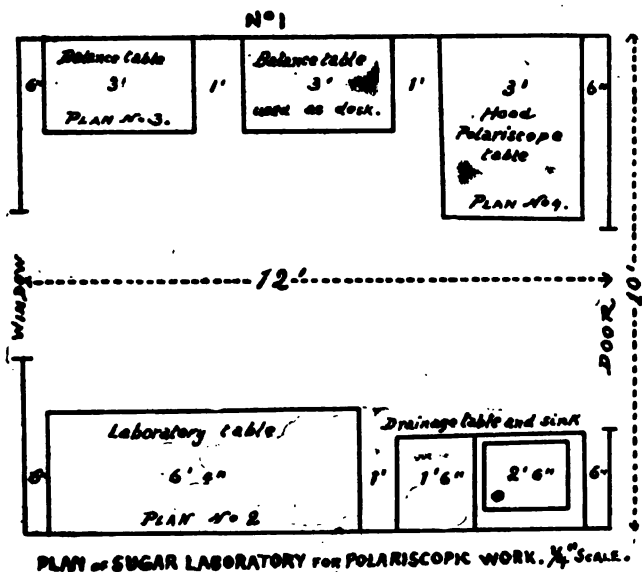
UNIVERSITY OF NORTH CAROLINA,
September 30th, 1891.

PLAN FOR SUGAR LABORATORY.*

BY EDGAR RICHARDS.

In presenting the following detailed plan for a sugar laboratory for polariscopic work, I have had in mind the need of a factory for some simple, and, as far as possible, inexpensive form of tables. I have made use of the plans and specifications I have already employed in fitting up the laboratories at Washington and at San Francisco. The elaborate gas, water and sewerage connections, as well as laboratory tables of these places have, however, been omitted, the plans herewith shown being for factories not supplied with gas, and where, consequently, kerosene or alcohol is used as a source of heat.

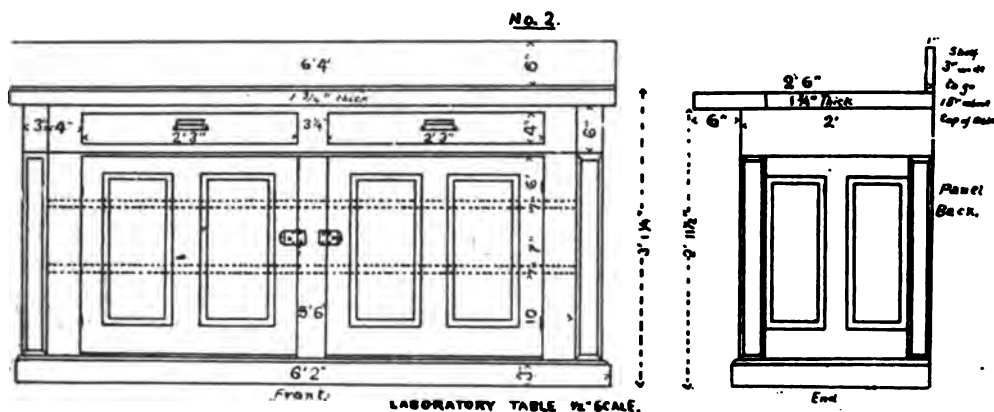
*From the Louisiana Planter, Sept. 19, 1891.



"The room used for the purpose should be one that is as far removed as possible from the vibration of machinery ; it should be well lighted and have some means of artificial heating, so that the temperature may be controlled, and should not be too near steam boilers, furnaces, flues, or any source of heat which could not be controlled. The polariscope should be placed in the darkest part of the room, and this part of the room may be darkened, if desired by curtains or hangings. In no case, however, should the polariscope be entirely separated from the room in which the rest of the work is performed, as the solutions should be made up and polarized at the same temperature. The lamp used for the illumination of the polariscope, on the other hand, should be separated from the instrument, as its heat tends to increase the temperature of the room and cause it to vary from time to time.

"The table upon which the polariscope stands should be level, and the instrument itself should not be near any source of heat, and should not be exposed to the direct rays of the sun.—Reg. S. 7, No. 17, S. No. 3.

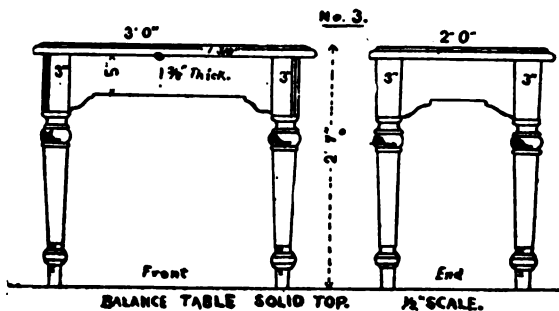
The separation of the lamp from the instrument is very effectively accomplished by the hood shown (No. 4), which makes a



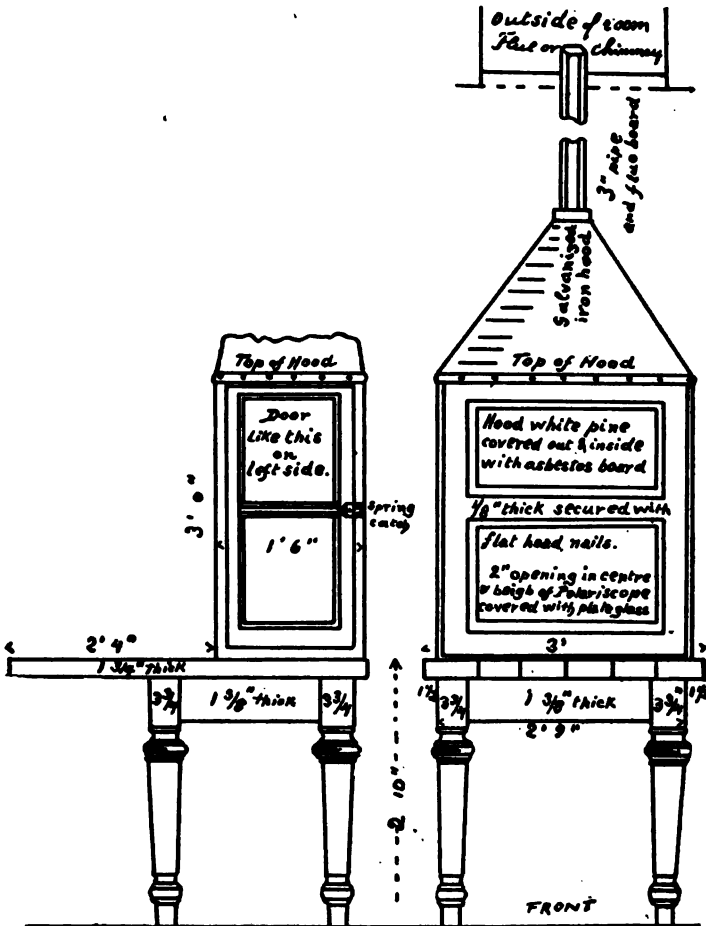
separate compartment for the lamp, the heat from which is carried off through the three-inch pipe outside the room. The lower partition should be perforated at the height of the instrument with a two-inch opening, which is covered by a piece of plate glass, thus preventing radiation and yet allowing the passage of the light. Both the in and outside of this part of the hood should be covered with asbestos board one-eighth of an inch thick, secured with flat-headed nails.

THE GENERAL PLAN, NO. 1.

The general plan, No. 1, drawn on a $\frac{1}{4}$ -inch scale, shows the general arrangement of the various furniture. A room 10x12 feet is about as small a space as will accommodate the necessary furniture, and allow the chemist elbow room. The balance table (No. 3)



should be placed nearer to the window,—a north or south exposure is preferable,—and next to it some sort of writing desk ; another balance table will do for this purpose as less expensive than a regular office desk, then the polariscope table with its hood (No. 4). The laboratory table (No. 2) is placed on the left side of the room. Some sort of a washing place should be placed near it ; this may consist of a porcelain-lined iron sink, covered with a 3-inch strip of wood on top, and having at one side a drainage



board sloping $\frac{1}{2}$ inch toward the sink so as to drain readily. The drainage board and top of sink would be much improved by being covered with sheet lead 4 pounds to the foot; the sink and board may be enclosed, thus giving additional storage room if needed. Water and steam can be connected with the laboratory sink, and the waste carried off. A board perforated with 3 rows of 2-inch holes, spaced diagonally 3 inches apart from centre, should be placed about 18 inches above drainage board, and should be 18 inches long. In it the flasks, funnels and other glassware can be placed to drain.

LABORATORY TABLE, NO. 2.

The laboratory table is made of white pine, 1 inch or $\frac{7}{8}$ inch stuff, stained red. It is $37\frac{1}{4}$ inches from floor to top of table. The top, which is made in three pieces of $1\frac{3}{4}$ inch stuff, glued together and fastened with screws to prevent warping, projects in front 6 inches beyond the general line of table, is 6 feet 4 inches long and 2 feet 6 inches wide. A decided improvement is to cover it with sheet lead, 4 pounds to the foot, as it is then readily kept clean. Otherwise it should be rubbed once a week with a heavy mineral lubricating oil, which readily deposits its paraffine among the pores of the wood. The drawers may be divided down the centre, and a partition, 2 inches wide, may be made toward the front, if desired. Two shelves in the cupboards will probably be ample. The back and sides of the table should be panelled to prevent warping, although tongue and groove stuff will do. The details are clearly given. Scale, $\frac{1}{2}$ inch = 1 foot.

BALANCE TABLE, NO. 3.

This table is 3 feet long by 2 feet wide by 2 feet 7 inches high, and requires to be solidly built. Top may be made of cherry, otherwise white pine, stained red. Scale, $\frac{1}{2}$ inch = 1 foot.

POLARISCOPE TABLE, NO. 4.

This table is 3 feet long by 3 feet 10 inches wide by 2 feet 10 inches high. The hood stands at the back. The top, of $1\frac{3}{4}$ inch stuff, is made up of from 4 to 6 pieces glued together, preferably of cherry, otherwise white pine stained red, and must be smooth

and level. Front of hood covered with asbestos as already mentioned. The hood has a door on left side whereby the source of light can be regulated. Scale, $\frac{1}{2}$ inch = 1 foot.

All these tables can be readily made by any cabinet-maker, and should not be very expensive. With such a laboratory, equipped with the necessary outfit and a good chemist, any sugar manufacturer, who can afford the expense, will find he has the means of properly controlling the waste of his factory, and consequently improve and increase his output.

MANUFACTURE OF CREAM OF TARTAR AND TARTARIC ACID FROM GRAPE POMACE AND WINE LEES.*

BY LOUIS PAFARELLI, BERKELEY, CAL.

The chief industry that finds its raw material in the by-products of the vintage and wine-making is without doubt that of the extraction of cream of tartar and tartaric acid. This industry when properly conducted is highly remunerative, and for that reason ought never to be neglected in a viticultural country.

According to the official reports of Italy, that country exported in 1887 \$5,000,000 worth of cream of tartar, and that sum could be quadrupled if all the raw material at disposal were utilized.

This industry has proved to be such a source of wealth, that the wine-makers no longer remain inert, and though every year the production of cream of tartar increases, it does not suffice to satisfy the foreign demand.

The nineteen wine-growing departments of France produce, yearly, from nine to ten million hectoliters of pomace, which are transformed into cream of tartar and tartaric acid.

Grape pomace constitutes one of the important products of wine-making. The mass which remains after pressing out the wine is a mixture of stems, skins and seeds in the following average proportions :

Stems	22.98
Skins	58.72
Seeds	18.30

*From a pamphlet sent by the author.

When stemming is practiced, as is usually done to make the wine less harsh, the proportions change as follows :

Skins	76.24
Seeds	23.76

Pomace which has undergone a complete fermentation is richer in alcohol and in cream of tartar than that in which the fermentation has been incomplete.

The larger part of the cream of tartar is found dissolved in the sweet liquid of the pulp, whilst a smaller part occurs in the crystalline state in the interior of the cells. The latter dissolves with difficulty, and remaining in the skins, is precipitated in the insoluble form. This precipitation is facilitated, in the first place, by the production of alcohol, which prevents the solution of the cream of tartar, and finally by the lowering of the temperature, which follows fermentation. A large part of the precipitated salt goes to form the lees, whilst a smaller portion is taken up by the pomace. It is precisely this portion that ought to be utilized in addition to that procured from the lees, for the annual production is so great that it should not be wasted, especially as the cream of tartar can be extracted after having distilled off all the brandy.

It should, however, be remembered that the pomace contains more cream of tartar before distillation than after, but it is always more advantageous to utilize it for both purposes.

The *lees* are the most important waste product of wine-making, and are generally utilized in the manufacture of tartaric acid ; the tartar from the pomace is more suitable for making the best cream of tartar.

The pomace produced in California contains from 3.7 to 7.7 per cent. of cream of tartar, and on the average it might be said that it would furnish about 5 per cent. But we must take into account the losses in the processes of manufacture ; therefore that average is diminished.

According to analyses made of the lees of several wines, red and white, by Mr. F. W. Morse, at the California Experiment Station, a minimum was found of 4.33, a maximum of 58.51 per cent. of cream of tartar.

Prof. Carpené, in his study of the tartars of the different provinces of Italy, reports the following data :

	Cream of Tartar.	Total Tartaric Acid.
Tartars	From 3.75 to 94.86 %	From 2.094 to 74.25 %
Lees from the first racking.	Traces to 64.61 %	From 4.70 to 62.80 %
Tartars from the distillation of pomace, Traces	to 93.12 %	From 27.30 to 75.23 %

Callegari, in Italy, having made analyses of both red and white wine lees, found the ratio to vary from 7.52 to 74.44 per cent. of cream of tartar. Braconnot in France in the lees of old wines found 60.75 per cent.

As these figures show, the quantity of cream of tartar contained in the lees of wine is somewhat variable, which results from several causes; it should be especially noted that the lees from the first rackings is less rich in cream of tartar than that obtained in subsequent rackings off; for the new wine not only deposits tartar, but also abundant quantities of nitrogenous matters, formed principally of dead and living ferments, vegetable debris from the grape stems, coloring matter, and fatty, pectic, gummy, mucilaginous substances, etc., the necessity of the elimination of which renders the purification of the cream of tartar difficult.

PRESERVATION AND TRANSPORTATION OF POMACE.

When operating on a large scale and with large quantities, receiving a portion of the raw material from other vineyards, the operations will extend over a considerable space of time, and it is essential to consider the preservation and transportation of the pomace.

It is worthy of remark that the pomace which has been preserved for some time, gives a larger proportion of brandy, the quality of which is, moreover, better, being more fragrant and agreeable.

There is also no loss of cream of tartar; on the contrary, it separates with greater facility during the extraction.

Nevertheless, the *proper preservation* of the pomace presents some difficulties.

The alcohol which it contains easily changes into vinegar, and if contact with the air is not perfectly prevented, mouldiness may appear, which would also spoil the cream of tartar.

To prevent, then, all deterioration of the pomace, it is taken

and packed into vats or trenches, with the precautions which we will point out later.

In practice, trenches are only useful when operating on large masses of raw material, whilst in working on a small scale, the pomace is packed into wooden vats. These are the best means of preserving the pomace; the use, however, of vats, which are destined for the fermentation of must, should be avoided.

The trenches should be rectangular in shape and well lined with cement. They should be of a depth of from $6\frac{1}{2}$ to 10 feet, and divided by walls, into compartments holding about 20 tons, calculating that, on the average, 10 tons of pomace well packed will occupy 40 cubic feet.

In any case, whether trench or vat is used, the pomace is packed in the same way.

The pomace, which should be well pressed and dry, and as cold as possible, should be well broken up with a fork or with the hand. It is spread out evenly and thoroughly tamped down. Instead of tamping, the same object may be attained with greater dispatch and ease, by using a heavy apparatus, which everyone can construct for themselves.

This work must be done quickly, and the maxim of not putting off till to-morrow what can be done to-day, strictly adhered to.

When all the pomace to be treated has been crumbled and packed as we have described, it should be covered with a layer of clay, of a thickness of from 2 to $2\frac{3}{4}$ inches, which should be well beaten down. After this, all that is necessary is to watch this covering, which is subject to cracking whilst drying. As soon as cracks are perceived, they should be filled up with some of the same clay, any pomace which has become mouldy being removed.

Pomace well preserved should retain a vinous odor; be dry to the touch, and without mould or taste of vinegar; otherwise it will produce inferior brandy and will not be good for the preparation of cream of tartar.

If all the preceding conditions are fulfilled, the grape pomace will keep for about five months, and in some cases even longer.

When the time to commence work arrives, the covering of clay is removed and the contents of the trench or vat used without delay.

The *transportation* of the pomace presents more difficulties than its preservation at the place of production.

It is always dangerous to ship the pomace in sacks, and the only way to avoid the danger is to place them in tight cars which can be filled with the vapor of sulphurous anhydride.

Transportation in wooden vats presents fewer difficulties, but it is more costly.

It is necessary to compress the pomace very much into these receptacles; and if, as is sometimes the case, it contains undecomposed glucose, the carbonic acid which is given off acts as an anti-septic.

The pomace might be wetted with a weak solution of sugar or of must (from 2 to 5 per cent.), and so, by fermentation, cause a liberation of carbonic acid.

Then to prevent all access of air through the pores of the wood, it would be well to coat the inner surface of the vats with some cheap substance, such as silicate of potash, much diluted, or with paraffine.

When the vat is full, a layer of straw is placed on top, then a cement of clay, and the whole covered with the wooden top pressed down.

* * * * *

EXTRACTION OF THE CREAM OF TARTAR.

To extract the cream of tartar, the pomace must be mixed with a certain quantity of water, the whole brought to the boiling point, and the boiling continued until the cream of tartar is dissolved.

When calculating the quantity of water necessary, the loss by evaporation during boiling should be taken into account; and also, that in contact with the pomace it dissolves other substances, which diminish its already small power of dissolving the cream of tartar.

However, knowing the solubility of cream of tartar in boiling water, for pomace containing about 5 per cent. of the salt about its weight of water would be needed. But in taking into account the losses of which we have spoken, it is necessary to employ three parts of water for two parts of pomace, diminishing the proportion of water accordingly for poorer pomace; the pomace must remain in contact with the boiling water for at least three hours.

(A) DISTILLATION APPARATUS OF COMBONI.

Divers methods have been invented for the complete utilization of the brandy and cream of tartar contained in grape pomace, but they are not all practicable ; either on account of their complexity and consequent high cost, or of some inconvenience which they present. The only method which satisfies all the conditions is that invented by Prof. Comboni of the Viticultural School of Conegliano, Italy, and his distillation apparatus is now commencing to be used on a large scale. The two principal parts, one for steam and the other for direct heat, which are distinguished by their perfect working and moderate price, were constructed principally with the object of having a model that would suit the needs of both the small and larger producer of wine, without obliging him to put in costly and expensive fixtures.

The Comboni's model compared with those that come from other countries, possesses practical and economical advantages of great importance.

The model for the use of direct heat is extremely simple, whilst possessing all the features necessary for the production of an article of a good commercial grade, without traces of fusel oil ; besides this, the time taken is only half that needed by all other systems known at present.

In this apparatus the idea has been put in practice of keeping the pomace half dry during the distillation and so out of contact with the heated part of the boiler. It is then a distillation by steam which is accomplished without the aid of a generator, as the lower part of the boiler produces the steam, whilst the upper part acts as still. Very interesting and peculiar is the part of the apparatus placed beside the boiler. In this part, which takes the form of a large tube, are contained the arrangements for concentration and condensation of the alcohol and for depriving it of fusel oil *without allowing the alcohol to return to the distilling boiler*; it comes out averaging 55 to 60 per cent., clean tasting and ready to be placed on the market.

No one else, so far, has invented an apparatus at once so simple and so complete, for the use of the vineyardist. On account of these advantages, one man can manage the distillation in a small space and without the deplorable confusion and disorder that is

always seen with the models for steam or for direct heat heretofore used.

The entire apparatus is composed of a furnace (square, rectangular or cylindrical), in which is placed at a third of its height, a slightly conical boiler, provided with a discharging tube, a level indicator, and a feed tube for water. The part of the boiler above the furnace is furnished with two or more wooden gratings, on which is placed the pomace, so that it is never submerged in the boiling water below.

The steam from the water passes through the pomace and deprives it of its alcohol, and then enters from below into the wide tube or cylinder, where it passes through the purifier and is deprived of its fusel oil, and then through the concentrator, from which it rises to the condenser and flows out.

An advantage which belongs exclusively to Prof. Comboni's apparatus, is that of an automatic, tubular refrigerator for the circulation of water, and which is capable of being taken to pieces, so that with the greatest ease, and without the help of a mechanic, it is possible to clean the refrigerating tubes; this has never been done before, even for large models which also have tubular refrigerators.

To the incontestable merits of Comboni's direct heat model must be added the moderate price of the apparatus, and the possibility not only of distilling pomace, but also wine or other liquids.

The steam model is also extremely simple; it is formed of a tubular generator, and therefore serves for steaming casks or any other application of steam, which communicates with one or several simple stills, from which the hydro-alcoholic vapors pass into the same rectifying apparatus that has been already described. With this model it is possible to obtain, if desired, alcohol of an average strength of 75 to 80 per cent. without a trace of fusel oil.

The distilled pomace is taken rapidly from the apparatus and introduced into a large boiler capable of containing the product of four distillations; at the same time the water, which has already served for the extraction of cream of tartar, is added in the proportion of one and a half part by weight of water to one part of pomace. This mixture is allowed to boil slowly for three hours, after which the mother liquor is drawn off from the bottom, passed

through a metallic filter, and received in small vats corresponding in capacity to the amount of liquid held by a cream of tartar boiler.

The dry pomace which is taken out by the opening at the bottom of the boiler can be used for manure or fodder.

(B) MONTAGNA'S METHOD.

The following is the method used by Mr. Montagna, near Rome, Italy, for extracting the cream of tartar from pomace :

After completing the distillation of the alcoholic matters, the pomace is placed alternately in two boilers with the necessary quantity of water, plain water first, afterwards "mother liquor," and boiled for eight hours, after which the liquid passes into two funnel-shaped wooden vats, in which hangs rows of small cords. Of course the liquid pressed from the pomace, after washing it several times with boiling water, is also put in the same vats. All this is allowed to cool for four days, when the mother liquor is run into a reservoir, from which it is pumped again into the boiler, together with a fresh quantity of pomace. 48 vats are necessary for carrying on the work without interruption. Three qualities of cream of tartar are obtained ; the best is taken from the strings, in the form of large, almost white crystals, and with very few impurities between them, and of a grade of 94 to 97 per cent.

The second quality is that deposited on the sides, and is formed of large and small crystals. It is rather redder than the preceding ; it is broken, washed with cold water, dried in the air, and placed, generally, with the first quality. The third consists of the deposit at the bottom of the vat, from which by decanting and washings with cold water the light organic matters are separated.

This kind of cream of tartar, which has the appearance of red sand, is put in casks set on their ends, from which are decanted, successively, the waters used in washing.

In operating with large quantities, the third quality may be washed by means of a centrifugal machine similar to a cream separator.

Mr. Montagna claims to have obtained from 100 kilos of pomace as much as 5 kilos of cream of tartar of the first two qualities, and

two kilos of the third ; generally he extracts an average of about 5 per cent.

(C) METHOD SUITABLE ONLY FOR OPERATIONS ON
A LARGE SCALE.

To obtain from the pomace alcohol of better quality, it is necessary, according to the experiments of Mr. Rommier, to submit the pomace to a methodical washing with water, as is done with beets in the manufacture of sugar.

In this case also, the apparatus of Prof. Comboni may be employed to distill the liquid resulting from the washing. This liquid, containing in general from 6 to 7 per cent. of alcohol, and even more, leaves after distillation a hot acid liquid very suitable for the extraction of the cream of tartar from the washed pomaces.

If coal is used, about 40 to 44 pounds will be needed on the average for 200 pounds of pomace.

The price of Comboni's apparatus is not only very reasonable, but it can be run by two workmen if it has one still, or by three if it has two or more stills.

In fact, in a country where labor is so dear, this will be found to be a means of economizing both time and money, whilst being sure of yielding good results.

Very often, in this method, the extraction of cream of tartar takes place in autoclaves warmed by steam and under a high pressure instead of in the ordinary boiler.

Before quitting the subject of the extraction of cream of tartar from pomace, it is very important to say a few words regarding some facts of great value in this industry.

It should be remembered that the pomace which has been used in the making of piquette has no value for the making of cream of tartar, and the more alcoholic the wine, the more cream of tartar the pomace contains. The higher the temperature and longer the boiling is continued, the more complete will be the separation ; cream of tartar being not changed by a temperature of 370 degrees F.

It is necessary, also, that the extraction of cream of tartar and its crystallization should take place in separate rooms ; for in that in which the former takes place the temperature would be favor-

able to tartaric fermentation, and there would be great risk of losing the entire product.

The germs of tartaric fermentation are carried by the air, and find a medium very favorable to their development at a temperature of 86 degrees to 95 degrees F. in mother liquors containing little acid ; for this reason care should be taken that their acidity is not lower than 8 pro mil.

Sometimes mould appears in the crystallizing vats, and as it is deleterious to the cream of tartar, it should be removed as soon as perceived.

The vats ought to present the largest possible cooling surface, and the mother liquor should be drawn off very slowly, in order to prevent its taking with it any of the crystals.

The method of crystallizing on strings must be abandoned, as it takes too much time. The deposited cream of tartar should be separated from the mother liquor as quickly as possible, and if dried in the sun it acquires a much finer appearance than if the drying took place by means of a stove.

The mother liquor ought not to be employed more than five or six times for the extraction of the tartar of the pomace ; the more acid the liquor, the better it is suited to the extraction of the tartar.

Finally, the greatest cleanliness should be maintained in the premises and utensils used in the manufacture.

OLIVE OIL ADULTERATION, AND HOW TO DETECT THE ADULTERANTS.*

BY PROF. LOUIS PAPARELLI, STATE UNIVERSITY, BERKELEY, CAL.
In charge of Viticulture and Olive culture.

Olive oil, which is the best of all oils, and largely used for alimentary, industrial, and medicinal purposes, on account of its higher price, tempts the cupidity of modern tradesmen. This is a serious evil, which contributes to diminish credit, occasion distrust, demoralizes commerce, raises up an infinity of law suits which are profitable only to lawyers, doing great damage to commercial houses, which, in spite of their circumspection, become sooner or later victims of these adulterations. And this deception

* From a pamphlet sent by the author.

of the merchant falls on the purchaser who in good faith believes he is buying a pure product, paying for it frequently a very high price.

It being, therefore, impossible to stop completely the evil, which is always increasing and menaces the true industry and the honest commerce of olive oil, it is better to confide in the means that science places at our disposal to detect the adulteration of the oil, and so discourage dishonest practices.

Happily, olive oil adulteration is rather limited ; olive oil cannot be made artificially like wine, but other oils, which have a certain analogy with it and are lower priced, can be partially substituted for it. Sometimes, but rarely, this valuable substance is mixed with oils, dangerous to health ; but in case the adulteration is made with oils, which on account of their properties are quite different from olive oil, the eye and nose can generally detect them easily. Of course, people not accustomed to seeing and using olive oil might be deceived, not only in such a case, but they might also accept as olive oil that made entirely from one or more other oils.

In any case, even when the adulteration is made with good oils from other plants, it disgusts the taste and the stomachs of persons accustomed to the use of the true olive oil, and at the same time the conservation of the oil is greatly compromised. Other bad results may be caused by frauds, when the oils are used for industrial purposes.

In the trade we find many kinds of olive oils, the tastes and qualities of which depend, within certain limits, upon many circumstances ; for instance, the variety of olive from which the oil was obtained, the manner and time at which the olives were picked, the method in use at the oil factory, etc., all of which are natural differences.

Oils are not single substances, but are mixtures of several substances furnished by nature, and the process of elaboration of which is, in large part, unknown. So we must not be astonished if in the analytical test the reactions are not always clear for the same oil, although given as characteristic and sure.

Olive oil is principally formed of a mixture of glycerids—palm-*itin*, *stearin*, *olein* ; and we may consider that the first two are in the proportion of 28 per cent., and the third 72 per cent.

The oils that are most frequently added to olive oil are cotton-seed oil, sesame oil, rape-seed oil, poppy-seed oil, and peanut oil. According to Secretary Lelong, other substances are used for the same purpose, but of them we will speak at a future time, when we shall have the occasion to study such adulterations. Therefore, when we receive an olive oil declared to be pure, we will have to solve the following questions :

Is it a pure olive oil? Is it an olive oil adulterated with cotton-seed oil? Or is it an olive oil adulterated with oils from other seeds?

In order to answer such questions, the examination of both the physical properties and the chemical reactions of the suspected oil is necessary ; and if in some cases one or two tests only may be sufficient to enable us to pronounce an opinion, in most cases we must submit the oil to all the tests recognized at present as characteristic and sure, and only from the whole of the results obtained can we decide upon the purity of the oil.

TESTS OF THE ADULTERANTS.

At first the physical characters of each sample must be examined, viz.: color, odor and taste. The two latter always give useful indications regarding the purity of an olive oil, but they can be only appreciated by an expert.

The specific gravity is also determined, although that of most seed oils does not differ much from that of olive oil. Those oils of which the specific gravity is quite different are generally not used for adulteration.

The point of fusion and of solidification of the free fatty acids, the caloric degree, the electrical conductivity of the oil, may be taken into account in the examination, but all these physical properties differ so little in the different oils most used for adulteration, that, although valuable in distinguishing one from the other, they are useless when the oils are mixed.

Therefore, we will give special attention to the chemical reactions now known as characteristic and quite sure for most cases.

IODINE ABSORPTION.

The iodine number is the quantity of iodine absorbed cold by a hundred parts of oil. About 0.3 gms. of oil are dissolved in 10

cc. of pure chloroform and mixed with 20 cc. of an alcoholic solution of iodine and chloride of mercury (25 gms. of iodine and 30 grams of chloride of mercury in 1,000 cc. of pure alcohol at 95 per cent.). The liquid, being in bottles well closed, is kept for about two hours in a cool and dark place. In the same conditions are kept another 20 cc. of the same iodine solution with 10 cc. of chloroform, and the strength of it is determined by a solution of hyposulphite of soda. The difference between the quantity of the hyposulphite employed to destroy the color of the iodine solution which has been in contact with the oil, and that needed to destroy the color of an equal quantity of iodine solution unmixed with oil, represents the iodine absorption of the oil.

According to different authors, the ratio of iodine absorption by olive oil may vary from 79 to 88, while most chemists do not admit more than 84.5 as a standard, and consider as adulterated every oil which passes the limit. But this test cannot be altogether relied upon because higher iodine absorption has been found for pure olive oils. The causes which produce this variability, so far as studied, are the following :

First—The more mature the olives are, the higher is the iodine absorption.

Second—Old and rancid oil has generally a slightly lower number.

Third—The method of oil making has also its influence ; oil from the pulp only shows slightly less iodine absorption than that obtained from grinding pulp and pits together ; oils extracted by chemical solvents have a lower iodine absorption than the same obtained by pressing ; oils obtained from pits always show a higher iodine absorption than those extracted from the fruit.

Fourth—It seems that the largest influence is due to the variety of olive from which the oil is made ; in fact, some varieties show a very high number. On the whole, the conclusion is that high iodine absorption, even up to 88, is not always indicative of the presence of seed oils, but may be on account of the quality of the oil itself. Therefore, to be able to judge if an olive oil might or might not be mixed with seed oils, we must take into consideration the other chemical tests, which give better results

BECHI'S REACTION.

This reaction serves to reveal the presence of cotton-seed oil in

olive oil, in seed oils, and even in cod liver oil. It may be briefly thus described :

An alcoholic solution of nitrate of silver is made in the following way :

Nitrate of silver	1 gram.
Alcohol at 98 per cent.	200 cubic centimeters.
Ethylic ether	40 cc.
Nitric acid	0.1 gram.

Another solution is also made of :

Amylic alcohol (fusel oil)	100 cc.
Pure colza oil (rape-seed oil)	15 cc.

The reaction is made in the following way : To 10 cc. of the oil to be tested add 1 cc. of the silver reagent, and 10 cc. of the solution of colza oil in amylic alcohol ; stir briskly and divide the mixture so obtained into two equal parts ; warm one-half for a quarter of an hour at the boiling point of water, and compare with the other half to see if there has been any change of color. In case of any addition of cotton-seed oil a dark, brownish-red coloration will be obtained. According to the author the same result may be obtained without using colza oil, but he employs it in order to obtain always a uniform coloration.

HAUCHECORNE'S REACTION.

Stir together briskly six grams of oil with two grams of pure nitric acid, and warm the mixture for twenty minutes in a bath of boiling water. Pure olive oil, treated in this manner, becomes somewhat pale, and if it is a dark colored oil assumes the proper yellow color of fine olive oils while it becomes yellowish orange or reddish brown if it contains any seed oils. In order to obtain good results it is necessary to operate always under the same conditions.

BRULLE'S REACTION.

To 10 cc. of oil add 0.1 gram of dried albumen in fine powder, and 2 cc. of nitric acid. Warm all carefully until the acid begins to boil, then stir well, continuing to warm until the albumen is completely dissolved. At this point the genuine olive oil becomes almost colorless, and after cooling it becomes more or less

turbid, but of a fine yellowish straw color which it retains for a long time. After twenty-four hours it becomes completely solid and remains of the same color. On the contrary, when seed oils are present the coloration is from yellowish orange to reddish brown at the time of the dissolution of the albumen by heating, and generally they do not solidify.

HEYDENREICH'S REACTION.

In a porcelain capsule, with a flat bottom, put enough concentrated and pure sulphuric acid to make a surface as large as a silver dollar, and on it let fall five or six drops of the oil to be tested. Observe carefully the coloration produced during three minutes at the point of contact of the oil with the acid. This coloration in pure olive oil should be yellowish, or greenish yellow, and in seed oils from yellowish orange to reddish brown. This reaction in some cases might produce an error, if not carefully practiced; and it is also necessary not to rely on that test alone, but to try others.

BAUDOUIN'S REACTION.

A very characteristic reaction of sesame oil is the property it has of turning crimson color a solution of sugar in concentrated hydrochloric acid. The reagent is prepared by dissolving 1 gram of sugar in 100 cc. of hydrochloric acid. To one volume of this solution add two volumes of the oil to be tested, and stir briskly for some time. After some minutes of settling, the aqueous liquid which separates is uncolored if any sesame oil is present, but in contrary case is colored crimson, more or less dark.

SCHNEIDER'S REACTION.

Colza, or rape-seed oil, like other oils of the crucifers, contains sulphur; therefore when carefully treated with silver nitrate, they produce a black coloration due to the formation of sulphide of silver. For this test dissolve the oil to be tested in two volumes of ether, and stir into the liquid about 5 cc. of a saturated alcoholic solution of nitrate of silver. After twelve hours allowed for settling, in a dark place, a black coloration or precipitate is obtained in case of the presence of oil from crucifers, especially after the evaporation of the ether.

THE PROPERTIES OF PRECIPITATES.*

BY E. WALLER, PH. D.

One division of Fresenius' book on *Quantitative Analysis* treats of "Forms," in which are given the properties of the various forms in which substances are separated for the purpose of weighing and determination.

It has seemed to the writer that those properties might be described in a manner more convenient for reference and also that there might be added the properties of various precipitates, etc., which are used in analytical work for purposes of *separation*. Of course, only those properties are considered which have a bearing on the usual manipulation of the different substances. For convenience the information has been grouped under the heads:

"*Remarks*" (*Rem.*), giving points not properly belonging under any of the succeeding heads.

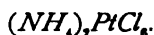
Conditions (*Cond.*), referring to the character of the solutions in which the separation can be made.

Solubilities (*Sol.*), under which the influences of different solvents which may be used in ordinary work are considered.†

Contaminants (*Contam.*), which is restricted to those substances only which would not be expected to precipitate if alone under the condition obtained.

Ignition (*Ign.*), or the behavior of the compounds designated on heating to a high heat in the way usually pursued with most of them. Under this head it is also necessary to consider the effect of ignition in contact with filter-paper or other carbonaceous substances indicated for brevity as "C."

A table is given which is intended to indicate at a glance the precipitates, etc., used and the forms in which they are weighed in case that is the object in view. Of course, the forms designated as for *weighing* can also be used for purposes of *separation*.



Rem.—Precipitant, $PtCl_4$

Yellow, perceptibly crystalline if formed slowly. Sometimes it

*School of Mines Quarterly.

†The terms "soluble" and "insoluble," as used in text-books of analytical chemistry are usually misunderstood by students. The terms are used in a relative—not in an absolute—sense, *e. g.*, when a precipitate is said to be "insoluble" the meaning usually is that under ordinary conditions of work, with a moderate bulk of solution, etc., the degree of solubility is so small that no material error is involved by regarding the separation as complete.

is dissolved from the paper by hot water into a weighed capsule, and the solution evaporated, thus avoiding the uncertainties involved in the use of weighed filters.

Cond.—Solution should contain only chlorides. Sodium salts only permissible. Solution should be cold, slightly acid, consisting chiefly of strong alcohol; an excess of PtCl_4 should be present.

Sol.—Somewhat soluble in cold, more so in hot, water. Fairly insoluble in strong alcohol, though more soluble than the corresponding potassium compound. Solubility in alcohol diminished by addition of ether. Its solubility also increases more rapidly by a rise in temperature or the dilution of the alcohol. Solubility increased by acid (HCl) or by alkali, diminished by PtCl_4 or Na_2PtCl_6 .

Contam.— NaCl which is not very soluble in alcohol. If sufficient PtCl_4 has been added to form Na_2PtCl_6 , the amount of contamination is small. The Na_2PtCl_6 crystals are more strongly colored and different in shape (needle-shaped) so that they can be readily detected. Can be removed by a short digestion with cold alcohol.

Ign.—Decomposed, leaving spongy platinum. Unless the heat is slowly raised some Pt may be volatilized with the products of decomposition.

KCl.

Rem.—Obtained by evaporation of the solution, and gentle ignition. Frequently, when in admixture with NaCl , the sum of the chlorides is thus obtained, and the KCl determined by PtCl_4 , the NaCl calculated, or the chlorine is determined and the proportions calculated. Salts containing K combined with acids capable of expulsion by HCl , may be evaporated with excess of HCl .

Cond.—Solution should contain only chloride or salt convertible into chloride by evaporation with HCl . Ammonia salts and such others as may be expelled by evaporation and gentle ignition may be present.

Sol.—Soluble in water, less so in alcohol or strong HCl .

Contam.— NaCl , see under remarks. If the solution has been long exposed to the air of the laboratory, it usually contains some

Element, Etc.	Purpose.	Obtained, or Precipitated as	Prepared for Weighing by	Weighed as
NH ₄	Weighing	(NH ₄) ₂ PtCl ₆	{ Drying Ignition	(NH ₄) ₂ PtCl ₆ or Pt
K	"	K ₂ PtCl ₆	{ Drying Drying or Ignition	K ₂ PtCl ₆ or Pt
	"	KCl	"	KCl
	"	K ₂ SO ₄	"	K ₂ SO ₄
Na	"	NaCl	"	NaCl
	"	Na ₂ SO ₄	"	Na ₂ SO ₄
Ca	"	CaC ₂ O ₄	{ " " "	CaSO ₄ CaCO ₃ CaO
Mg	Separation	CaCO ₃	"	Mg ₂ P ₂ O ₇
	Weighing	MgNH ₄ PO ₄	"	
	Separation	Mg(OH) ₂	"	
Ba	Weighing	BaSO ₄	"	BaSO ₄
	Separation	BaCO ₃	"	
Fe	Weighing	Fe ₂ (OH) ₆	"	Fe ₂ O ₃
	Separation	Fe(OH) _n (C ₂ H ₃ O ₂) _{en}	"	
Al	Weighing	Al ₂ (OH) ₆	"	Al ₂ O ₃
	"	Al ₂ (PO ₄) ₃	"	Al ₂ (PO ₄) ₃
	Separation	Al ₂ (OH) _n (C ₂ H ₃ O ₂) _{en}	"	
Cr	Weighing	Cr ₂ (OH) ₆	"	Cr ₂ O ₃
Ti	"	H ₂ TiO ₃	"	TiO ₂
	Separation	Na ₂ TiO ₃	"	
Zn	Weighing	2ZnCO ₃ ·3Zn(OH) ₂	"	ZnO
	"	ZnNH ₄ PO ₄	{ " " "	Zn ₂ P ₂ O ₇ ZnNH ₄ PO ₄
	Separation	ZnS·H ₂ O	Drying	
Mn	Weighing	2MnCO ₃ ·H ₂ O	Ignition	Mn ₂ O ₃
	"	MnNH ₄ PO ₄	"	Mn ₂ P ₂ O ₇
	Separation	MnO ₂	"	
Ni	Weighing	Ni(Electro)	Drying	Ni
	"	Ni(OH) ₂	{ Ignition	NiO
	"	Ni ₂ (OH) ₆	"	
	Separation	NiS·H ₂ O	"	
Co	Weighing	6KNO ₃ ·Co ₂ (NO ₃) ₆	Ignition	3K ₂ SO ₄ + 2CoSO ₄
	Separation	CoS·H ₂ O	"	
Cu	Weighing	Cu(Electro)	Drying	Cu
	"	Cu(OH) ₂	Ignition	CuO
	"	CuS	"	Cu ₂ S
Pb	Weighing	PbSO ₄	Ignition	PbSO ₄
	"	PbCrO ₄	Drying	
	Separation	PbS	"	
Ag	Weighing	AgCl	Ignition	AgCl
As	"	As ₂ S ₃	Drying	As ₂ S ₃
	"	MgNH ₄ AsO ₄	Ignition	Mg ₂ As ₂ O ₇
Sb	"	Sb ₂ S ₃	{ Ignition Drying	Sb ₂ O ₃ Sb ₂ S ₃
Sn	"	{ H ₁₀ Sn ₂ O ₁₅ SnS ₂	{ Ignition	SnO ₂
S ₂ SO ₂ S ₂ O ₃ SO ₂ , etc.	{ Weighing	BaSO ₄	"	BaSO ₄
P ₂ P ₂ O ₅ , etc.	Weighing	MgNH ₄ PO ₄	"	Mg ₂ P ₂ O ₇
	Separation	12MoO ₃ ·(NH ₄) ₂ PO ₄ + Na ₂ CO ₃ ·K ₂ CO ₃ , etc.	{ Absorption	Na ₂ CO ₃ ·K ₂ CO ₃ , etc. or Na ₂ CO ₃ + CaCO ₃
C, CO ₂ , etc.	Weighing {	or Na ₂ CO ₃ + CaCO ₃	"	
		BaCO ₃	"	BaSO ₄
Si & SiO ₂	"	xH ₂ O·SiO ₂	Ignition	SiO ₂
Cl	"	AgCl	"	AgCl
N & HNO ₃	Measuring	N or NO	"	
	Titration	NH ₃	"	
	Weighing	(NH ₄) ₂ PtCl ₆	"	(NH ₄) ₂ PtCl ₆ or Pt

organic dust, which carbonizes by ignition, requiring filtering and re-evaporation.

Ign.—Decrepitates somewhat unless dried for some time. Fuses at a low red heat, and volatilizes at temperatures a little higher, a small amount of caustic alkali being usually formed at the same time.



Rem.—Obtained by evaporation of the solution, or by adding H_2SO_4 to solutions containing combinations with volatile acids (chloride, nitrate, acetate, etc.), evaporating and igniting. In cases of admixture with Na salts, processes similar to those indicated under KCl may be used.

Cond.—Salts forming non-volatile sulphates, or containing non-volatile acids (H_3PO_4 , etc.), should be absent.

Sol.—Moderately soluble in water; much less so in alcohol.

Contam.— Na_2SO_4 , or other non-volatile sulphates.

Ign.—Practically non-volatile in the heat of an ordinary Bunsen burner if the heat is not unnecessarily prolonged. Where the solution has contained an excess of H_2SO_4 , some undecomposed $KHSO_4$ always remains, which can be best decomposed, or converted into K_2SO_4 by heating with a few lumps of solid ammonium carbonate. Ignited with C, K_2S may be formed. The conditions usually obtained, however, do not afford this result.



Rem.—Precipitant, $PtCl_4$.

More strongly colored than the corresponding ammonium salt, but otherwise resembling it in general characters. Like that compound, it is sometimes dissolved in hot water, and the solution evaporated in a weighed capsule, so as to dispense with weighed filters.

Cond.—Solution should be cold, alcoholic, and should contain, preferably, only sodium salts other than KCl. Chlorides or HCl should be present. Small amounts of Mg or Ca are permissible, though disadvantageous.

Sol.—Somewhat soluble in cold, more so in hot water. Insoluble in strong alcohol and in ammonium salts. Solubility increased by acid or alkali, diminished by $PtCl_4$ or Na_2PtCl_6 .

Contam.—NaCl and other salts (as sulphates) not soluble in

alcohol. Such contaminants are most readily removed by washing with aqueous solution of NH_4Cl , previously saturated with K_2PtCl_6 .

Ign.—Alone, it is imperfectly converted to KCl and spongy platinum; with a reducing agent (as $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), the conversion is complete. The heat should not be too rapidly raised. If ignited in platinum, too high a heat may fuse the finely divided metal to the platinum vessel. After ignition, the KCl formed must be washed off with water before weighing.

NaCl.

Rem.—See *Rem.* under KCl .

Cond.—As for KCl .

Sol.—Soluble in water; much less so in strong HCl or alcohol. Less soluble in these menstrua than KCl .

Contam.— KCl (see KCl) or other non-volatile salts.

Ign.—Decrepitates violently on heating unless very thoroughly dried. Fusible at full red heat, and volatilized at a temperature but little above its point of fusion. The temperatures of fusion and volatilization are, however, perceptibly higher than with KCl . Becomes slightly alkaline on fusion from loss of Cl .

Na₂SO₄.

Rem.—The suggestions as to K_2SO_4 throughout are applicable also to Na_2SO_4 (see K_2SO_4) even to the formation of NaHSO_4 by evaporation with excess of H_2SO_4 and ignition.

CaC₂O₄.

Rem.—Usual precipitant $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The solution of the reagent had best be boiling hot when added. Precipitated cold or in very dilute solutions, it separates in a very fine powder. In any case, boiling for a short time and then adding a few drops of ammonia is advisable before proceeding to filter. If precipitated in boiling alkaline solution, the solution bumps vigorously. Enough oxalate should be added to convert all Mg present into $\text{Mg}_2\text{C}_2\text{O}_4$.

Cond.—Best precipitated in a boiling neutral solution, which should contain only Mg and alkalies besides the Ca .

Sol.—Dissolved by mineral acids, slightly soluble in acetic. Somewhat soluble in MgCl_2 . Insoluble in MgC_2O_4 . From its

solutions in mineral acids, ammonia or other alkalies precipitate it unchanged.

Contam.— MgC_2O_4 which is removed by re-solution in HCl and reprecipitation by ammonia. If the proportion of Mg present is large this re-solution and reprecipitation may have to be repeated two or three times. Precipitating in a solution *barely acid* with HCl is most effective in separating from Mg .

Ign.—Affords first CaCO_3 , afterward CaO . Under ordinary circumstances the product is a mixture of the two. To obtain CaO it is necessary to ignite for some time over a blast-lamp. To obtain CaCO_3 , it is ignited moderately, and repeatedly moistened with ammonium carbonate and gently ignited after each addition.

Ignited with H_2SO_4 it affords CaSO_4 , which is frequently partially reduced to CaS by ignition with C , requiring further treatment with H_2SO_4 and ignition. The easiest mode of management is to transfer the filter paper containing the precipitate still wet to an ordinary fusion crucible, and wet down with concentrated nitric and sulphuric acids. Then expel the excess of acid with a gentle heat, and finally ignite. A second treatment with H_2SO_4 is often necessary. Instead of H_2SO_4 , a strong solution of $(\text{NH}_4)_2\text{SO}_4$, containing free ammonia and about 2 gms. NH_4Cl per 100 cc., has been recommended (*vid.* Crooke's *Select Methods* 2d ed., p. 47).

CaCO_3 .

Rem.—Usual precipitant $(\text{NH}_4)_2\text{CO}_3$. For separation or determination of CO_3 , the reagent is CaCl_2 with ammonia. Usually obtained for separation. At first it separates in flocculent or amorphous form, but after a short time assumes a crystalline form. This change is hastened by warming gently.

Cond.—Large proportions of alkaline salts, especially citrates, and of magnesium salts should be avoided. An alkaline solution is, of course, necessary.

Sol.—Soluble in water containing CO_2 ; very soluble in all acids; decomposed and dissolved by NH_4Cl , slowly in the cold, quickly if hot. Insoluble in water containing ammonium carbonate with ammonia.

Ign.—Converted to CaO as described under CaC_2O_4 . The change is more readily effected if some carbon is mixed with it.



Rem.—Usual precipitant for Mg— Na_2HPO_4 ; for P_2O_5 (ortho) —“magnesia mixture,” preferably that made with MgCl_2 .

Should be crystalline; if flocculent, some contaminant is present. When the proportion of precipitate which can form is small relatively to the bulk of the solution, some hours are necessary for complete separation.

Completeness of precipitation much accelerated by cold and agitation.

When washed as usual with diluted ammonia, alkaline phosphate Na_2HPO_4 , etc.) is not very rapidly removed, the salt being less soluble in ammonia than in water.

Cond.—Absence of silica or any bases other than alkalis. NH_4Cl or ammonium salts should be present.

Sol.—Solution should be cold for precipitation and filtration. Soluble in acids, even when weak, in hot solutions and, to some extent, in cold water; insoluble in dilute ammonia.

Contam.—Silica and $\text{Mg}(\text{OH})_2$, or basic salts of Mg. The latter is only likely to occur when the precipitate is used for the purpose of determining P_2O_5 or P. The difficulty is avoided by adding the Mg mixture (preferably the chloride) slowly with stirring. Silica may be weighed and deducted after ignition, weighing and dissolving in acid. MoO_3 may also occur when the molybdate separation has preceded.

Ign.—Should be well dried before igniting. If heated too rapidly some loss may result from too rapid decomposition. If the filter paper is allowed to burn with flame, some particles of the precipitate (in weighable amount) may be mechanically carried off. The precipitate has afterward a tendency to sinter together at a moderately high heat, thereby preventing the oxygen of the air from penetrating the mass and oxidizing the carbon, the precipitate being left gray or black. The best mode of managing is to expose the precipitate for some time to a dull red after the carbonization of the paper, and finally, finish with the full heat of the Bunsen burner. If the precipitate comes black, repeated moistening with nitric acid and cautious ignition is to be recommended.

$Mg(OH)_2$.

Rem.—Usual precipitant $Ba(OH)_2$ for separation from alkalis when these are to be determined. The $Ba(OH)_2$ should be tested for $NaOH$, which is not infrequently present.

Cond.—Alkaline solution moderately concentrated, containing no NH_4 salts.

Sol.—Dissolved by acids or ammonia salts. Precipitation partly prevented by presence of organic salts, citrates, tartrates, sugar, etc.

Contam.—Usually unimportant, the object generally being to remove from the solution MgO and all substances except those readily separable by ammonium carbonate.

 $BaSO_4$.

Rem.—Precipitant for SO_4 — $BaCl_2$; for Ba — H_2SO_4 .

Precipitated in an extremely fine state of division (runs through filter paper) if formed in cold or dilute solutions, or such as contain ammonia salts. Forms slowly if small in amount.

The tendency of the precipitate to creep up the side of a beaker may be checked by adding a drop of HCl .

Cond.—Hot solution acidified with HCl . Hydro-fluo-silicic acid or silica should be absent, also large proportions of calcium salts, or salts of the $(NH_4)_2S$ group of bases.

Sol.—Soluble in concentrated H_2SO_4 , in HCl when moderately strong and hot, and in HNO_3 even when tolerably dilute. It is also soluble in hot $FeCl_3$, in alkaline and alkaline earth nitrates, citrates, and salts of some other organic acids.

Insoluble in water, in (very) dilute HCl , and in acetic acid.

Contam.—The especial difficulty with $BaSO_4$ is its tendency to carry with it other substances, as alkaline, and alkaline earth nitrates, chlorates, sulphates and chlorides. Potassium salts give more trouble in this respect than sodium salts. The precipitate may also contain silica, and basic ferric, aluminic or chromic compounds.

Repeated boiling up with very dilute HCl , assists in removing some of these to a considerable extent, though there is some danger of dissolving some of the precipitate by this treatment. Washing alternately with hot dilute HCl , and with cold water, is often advantageous. Stolba's method of purifying the precipitate con-

sists in digesting (after washing) for ten to fifteen minutes at a boiling-heat, with 40 to 50 cc. of cold saturated solution of Cu ($C_2H_3O_2$), and acetic acid, filtering and washing free from Cu (*vid.* Crooke's *Select Methods*, 2d ed., p. 492). Sloane recommends for purification from iron, to decant the supernatant liquid closely, then add 5 or 10 cc. of concent. HCl, and boil for one minute, dilute, and after nearly neutralizing with ammonia, filter and wash thoroughly (*Jour. Am. Chem. Soc.*, iii., 37). Archbutt advises to precipitate warm (not boiling), allow to stand until thoroughly cold, and the precipitate has settled well, then to filter and wash with cold water (*Jour. Soc. Chem. Ind.*, ix., 25). Jannasch and Richards assert that no correct determination of SO_3 can be made in the presence of Fe, because the precipitate always contains more or less of a double barium iron sulphate, from which SO_3 is expelled on ignition. To avoid errors they therefore recommend the previous removal of the iron by ammonia (*Jour. Pr. Chem.* [2], xxxix., 321), (*vid.* also Lunge, *Zts. angew. Chem.*, 1880, 473). Ziegeler (*Pharm. Centr.*, 1881, p. 555) recommends the addition of some $AgNO_3$ to the solution (containing chloride) that the $AgCl$ may enclose, and carry with it the particles of $BaSO_4$. After washing with water the $AgCl$ may be dissolved off with ammonia.

Ign.—With C some BaS invariably forms. The difficulty may be remedied by adding a few drops of fuming HNO_3 to re-oxidize the S, and igniting again, or better by re-igniting after the addition of a drop or two of conc. H_2SO_4 .

BaCO₃.

Rem.—At first amorphous, it assumes almost immediately the crystalline form in which condition it does not affect alkalimetric indicators.

Cond.—Alkaline solution.

Sol.—Soluble in water containing CO_2 and in acids. Also taken into solution by NH_4Cl and some other ammonium salts, especially on boiling. Insoluble in a mixture of ammonium hydrate and carbonate.

Contam.— $MgCO_3$ if much is present, and carbonates of fixed alkalies if present.

Ign.—Converted imperfectly to BaO , unless mixed with carbon, when the change occurs readily.



Rem.—Precipitation in most cases effected by NH_4OH .

When but little ferrous iron is present, and heat is applied, a finely-divided red ("brick-dust") precipitate separates, which is insoluble except in concentrated HCl .

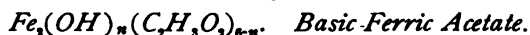
In presence of a larger proportion of ferrous salt, black $\text{Fe}_2(\text{OH})_6 = \text{Fe}(\text{OH})_2$, $\text{Fe}_2(\text{OH})_6$ will separate. With more ferrous salt the precipitate is green, the color being lighter the larger the proportion of ferrous salt; and when the iron is all absolutely in the ferrous form, the precipitate is white. Whenever ferrous salt is present, a double ammonium ferrous salt forms, which remains in solution, from which the iron slowly precipitates by absorption of oxygen, and conversion to the ferric form. NH_4Cl favors the precipitation of $\text{Fe}_2(\text{OH})_6$.

Cond.—Iron should be in ferric form. H_2S should be absent.

Sol.—Soluble in acids and in solution containing citric, tartaric acids, etc., as well as other organic substances, glycerine, sugar, etc. Insoluble in alkalis.

Contam.—Basic ferric salts, especially basic sulphate, unless the precipitant is in moderate excess. When precipitated by fixed alkalis, the precipitate contains some alkali, which is washed out with great difficulty. Precipitate will carry with it phosphoric acid as $\text{Fe}_2(\text{PO}_4)_2$ in nearly sufficient quantity to form that compound. The excess of phosphoric acid will remain in solution unless some other base (Al , Ca , etc.) is present to carry it down in combination. Precipitate may also contain nearly if not quite all of the Al , Mn and silica present. Mg , Co , Ni , Zn and Cu are also liable to be present in the precipitate, Ca also as CaCO_3 if the alkaline solution has absorbed any CO_2 from the atmosphere. From these latter (Mg , etc., including Ca), the precipitate may be freed by one or more resolutions and reprecipitations.

Ign.—Converted to Fe_2O_3 . With C , a partial reduction to Fe_3O_4 may occur. Fe_2O_3 is restored by adding a few drops of HNO_3 , and reignition. In contact with NH_4Cl , may form volatile Fe_2Cl_6 .



Rem.—Ferrous salts, if present, are not precipitated. If in very small proportion, they may induce the formation of the "brick-dust" precipitate alluded to under $\text{Fe}_2(\text{OH})_6$. In analysis of iron-

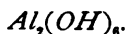
ores and manufactured irons, the reduction of the major part of the iron to the ferrous form, and application of the basic acetate, separation is frequently resorted to in order to remove the excess of iron, before determining phosphorus.

Cond.—The *dilute* solution should contain but little free acetic acid. The (ferric) iron should be in the form of acetate. This is obtained by neutralizing the free mineral acid present and adding $\text{NaC}_2\text{H}_3\text{O}_2$. No precipitate should appear in the cold, but on boiling a few minutes (three to five) it separates completely, provided, not too much free acetic acid is present. *Too long boiling* causes the precipitate to assume a form which filters with some difficulty.

Sol.—Soluble in cold dilute acetic acid and in mineral acids, also in citrates, and other organic substances mentioned as solvents of $\text{Fe}_2(\text{OH})_6$.—Insoluble in hot acetic acid only when quite dilute.

Contam.—Salts of fixed alkalis. Silica, alumina salts, and P_2O_5 , the latter in the form of $\text{Fe}_2(\text{PO}_4)_3$ [see $\text{Fe}_2(\text{OH})_6$]. The precipitate may also contain some Mn, Zn, Ni, Co or Cu. Mn is more likely to be present if the amount of $\text{NaC}_2\text{H}_3\text{O}_2$ added was large. The amounts of these last in the precipitate is much diminished by increasing the proportion of free acetic acid in the solution. The danger of having sufficient free acid to prevent the precipitation of all the iron is, however, considerable. By redissolving in HCl, neutralizing, adding $\text{NaC}_2\text{H}_3\text{O}_2$, and reprecipitating, the Zn, Ni, etc., can be removed. Zn usually gives the most trouble. If much is present, it may be advisable to precipitate in a solution containing enough free (acetic) acid to hold a little Fe in solution. The latter may be separated by evaporating the excess of acid from the filtrate. SiO_2 and Cu should be previously removed by known methods, if their presence in the precipitate will influence subsequent work.

When chromium is present in the solution, the action is peculiar. When iron predominates decidedly, all of the chromium is precipitated with it. If the ratio of chromium to iron is nearly the same, not only much of the chromium, but some of the iron is retained in the solution.



Rem.—In general terms the precipitate is very similar to $\text{Fe}_2(\text{OH})_6$, but is more easily prevented from forming, and when

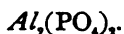
separated, being more gelatinous in character, is less readily managed. Usual precipitant, ammonia. A good method of managing consists in rendering slightly alkaline with ammonia, and passing H_2S , raising the temperature at the same time gradually to boiling.

Cond.—Neutral or slightly alkaline solution, containing preferably NH_4Cl .

Sol.—Dissolves in acids, and in fixed caustic alkalies; somewhat soluble in ammonia, especially in the cold. From this solution it may be separated by boiling out the major part of the NH_3 , particularly if NH_4Cl is present. Precipitation prevented by presence of tartrates, citrates, sugar, glycerine, etc. After boiling or standing for a short time, the precipitate will dissolve in acids (even HCl) slowly and with some difficulty.

Contam.—Basic Al salts, especially the sulphate. Retains P_2O_5 in proportion sufficient to form $Al_2(PO_4)_3$. May also contain Fe, Mn or SiO_2 (hydrated). Possibly, also, Mg, Zn, Co, Ni, Cu, etc., from which last it may be freed by resolution and reprecipitation except, perhaps, in the case of Zn, from which a complete separation of $Al_2(OH)_6$ can scarcely be effected. Ca may also accompany it as $CaCO_3$, if the alkaline solution has absorbed CO_2 .

Ign.—Converted to Al_2O_3 . Ignited with NH_4Cl some volatile Al_2Cl_6 may form. After ignition practically insoluble in HCl . Converted to a soluble form by fusion with an alkaline flux.



Rem.—Of service in the determination of Al in manufactured irons and in mineral phosphates.

Cond.—Fe, if present, should be in the ferrous form. The conditions usually produced are a solution acid with acetic, in which Fe has been reduced by $Na_2S_2O_3$, and containing an excess of alkaline phosphate. This is boiled for some time.

Sol.—Dissolves in mineral acids. Insoluble in moderately strong HCl , H_2O_2 . Prevented by tartrates, citrates, etc., in the same way as $Al_2(OH)_6$.

Contam.— $Fe_2(PO_4)_3$ and possibly basic ferric salt. If Fe is kept entirely in the ferrous condition (which is not always possible) this contamination would not occur. Remedied by redissolving, reducing and reprecipitating. $Ca_3(PO_4)_2$ (or alkaline salts if the solution is not sufficiently dilute) may also accompany the precipitate.

Remedy by resolution and reprecipitation. Glaser's method for mineral phosphates involves the previous separation of the lime, as CaSO_4 , by the aid of alcohol (*Zeit. angew. Chem.*, 1889, p. 636).

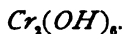


Rem.—Very similar to the corresponding Fe compound. Being more slimy in character, it gives more trouble in filtering and general management. Used for separation only.

Cond.—The same as for the Fe compound. Practically no free acetic acid is admissible. Al should be in the form of acetate. Precipitate obtained by boiling. If boiled too long, it filters and washes with more difficulty.

Sol.—Dissolves in acids, to some extent in very dilute boiling acetic. If the solution after boiling is allowed to cool, a considerable proportion redissolves. Soluble, or precipitation prevented by citrates, tartrates, etc. The small amount almost invariably remaining in the filtrate may be recovered by careful neutralization and boiling, or better by evaporating to dryness, and taking up with dilute acetic.

Contam.—As for the Fe compound. Salts of fixed alkalies, P_2O_5 [in proportion sufficient to form $\text{Al}_2(\text{PO}_4)_3$], SiO_2 (hydrated), Mn, Zn, etc.



Rem.—In general properties this precipitate resembles $\text{Al}_2(\text{OH})_6$ and its management is similar. Its tendency to carry with it other substances, requires that it shall always be redissolved and reprecipitated with ammonia at least twice.

Cond.—Absence of members of $(\text{NH}_4)_2\text{S}$ groups and preferably of all non-volatile salts. Solution must be exactly neutral (ammonia added in slight excess and then boiled until neutral). NH_4Cl assists the separation.

Sol.—Dissolves in all acids, in fixed alkaline hydrates and perceptibly in excess of NH_4OH . Soluble or prevented from precipitating by tartrates, citrates, sugar, etc.

Contam.—Salts of fixed alkalies, alkaline earths, members of the $(\text{NH}_4)_2\text{S}$ group, etc. (See above, *Rem.*)

Ign.—Converted to Cr_2O_3 , in which form, if strongly ignited, it becomes insoluble in HCl . In presence of fixed alkalies or alka-

line salts and in contact with the oxygen of the air, is partially or entirely converted to chromate.

H₂TiO₃ or Titanic Acid.

Rem.—Two forms, one tolerably easily soluble in acids, the other insoluble, except in very strong acids or by fusion, are known to exist. The "insoluble" form is obtained by boiling the solution acidified with sulphuric. The small amounts of phosphoric acid present in iron ores and other minerals interfere somewhat with the complete separation on boiling.

Cond.—Dilute solution containing but little free H₂SO₄. HCl and chlorides should be absent. Long boiling is necessary, the bulk of the solution being maintained. Fe, if present, should be in the ferrous form. HC₂H₃O₂ favors the precipitation. The best conditions for the separation of titanitic acid are boiling an acetic acid solution reduced by SO₂.

Sol.—The soluble form is attacked by the same solvents as Fe₂(OH)₆. The "insoluble" form is slowly soluble in hot concentrated HCl or H₂SO₄, or by fusion with KHSO₄.

Contam.—Fe₂O₃, Al₂O₃, SiO₂ and P₂O₅. Some iron inevitably is converted to Fe₂O₃, and separates with the precipitate. By resolution, reducing and re-precipitation, almost all can be removed. Al₂O₃ is prevented from contaminating the precipitate by the larger proportion of free acid. SiO₂ may be expelled after ignition by treating with HF (or NH₄F) and H₂SO₄. P₂O₅ by fusion, for some little time, with Na₂CO₃, and washing with dilute Na₂CO₃ solution, which leaves behind Na₂TiO₃, soluble in acids.

Ign.—Converted to TiO₂. Retains some SO₂; removable by adding a few pieces of solid ammonium carbonate and re-igniting. Volatilized by ignition with HF, alone or with an insufficient amount of H₂SO₄.

(xNa₂O, TiO₂)Na₂TiO₃. Sodium titanate.

Rem.—Usually obtained by fusing material containing TiO₂ and P₂O₅ for some time, to convert them into sodium salts, and then to separate them by lixiviation. Chiefly of service as a step in the determination of phosphorus in titaniferous ores.

Cond.—Long fusion at a fairly high temperature is necessary. A repetition of the fusion of the portion insoluble in water with a

fresh lot of sodium carbonate, is at least necessary in order to prove the efficiency of the first fusion.

Sol.—Dissolved by acids; to some extent by water alone. Insoluble in solution of Na_2CO_3 . The washing (leaching) of the insoluble portion should be continued until the washings begin to run cloudy.

Contam.—As usually applied to iron ores or precipitates from solutions thereof, the insoluble residue may contain besides sodium titanate, Fe_2O_3 , acid sodium silicates, alkaline earth carbonates, etc.

$2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$. *Basic Zinc Carbonate.*

Rem.—Usual precipitant, Na_2CO_3 . Flocculent at first, becoming more granular by boiling.

Cond.—Solution should not contain caustic or bicarbonated alkalis or any ammonia salts. If CO_2 is evolved by addition of the reagent, it must be boiled out. Only fixed alkalis besides the zinc should be present.

Sol.—Dissolved by dilute acids, fixed caustic alkalis, bicarbonates and ammonia salts; also by organic solutions. A very large excess of fixed alkaline chlorides hinders or partially prevents the precipitation. Insoluble in water and small amounts of fixed alkaline carbonates.

Contam.—Alkaline carbonate, necessitating several washings by decantation with boiling water to remove it. Fe_2O_3 , Al_2O_3 , SiO_2 . By dissolving the precipitate in HCl after ignition, Al_2O_3 and SiO_2 are left insoluble; on precipitating the solution with ammonia, redissolving and reprecipitating two or three times, $\text{Fe}_2(\text{OH})_6$ is separated. These impurities may then be ignited, weighed and deducted.

Ign.—Converted to ZnO , which in itself is not volatile. In contact with C or reducing substance, metallic zinc which is volatile may be formed.

ZnNH_4PO_4 .

Rem.—Usual precipitant, $\text{NaNH}_4\text{HPO}_4$. Some prefer Na_2HPO_4 in presence of ammonium salts. The best method of procedure is to add the alkaline phosphate to the acid solution and then to neutralize the hot solution by adding ammonia, little by little, finally to heat, immersing the beaker in a boiling water bath,

until free NH_3 is expelled and the precipitate is crystalline. The solution containing the precipitate cannot be boiled without bumping vigorously. The precipitate can be dried at 100° and weighed as ZnNH_4PO_4 or ignited and weighed as $\text{Zn}_3\text{P}_2\text{O}_7$.

Cond.—Oxalates should be absent. Large excess of ammonium chloride or acetate should be particularly avoided. Practically, the solution should only contain alkalies besides the zinc.

Sol.—Dissolved by acids, excess of ammonia, ammonium oxalate chloride or acetate, especially if hot. The solvent effect of the chloride and some other ammonium salts is to a very great extent diminished by the use of an excess of alkaline phosphate (about three times as much as is required to afford the compound).

Ign.—If heated up too rapidly, some loss may be experienced. In contact with C, a partial reduction to metal and consequent loss may occur. The precipitate should be carefully separated from the filter paper and the same burned separately, or it may be dissolved by means of dilute nitric acid into a weighed capsule and the solution evaporated and finally ignited.

After ignition the precipitate is usually opaque, white, somewhat sintered together; sometimes, without apparent reason, it fuses to a glass.

$\text{ZnS.H}_2\text{O}$.

Rem.—Usual precipitant, H_2S in neutral solution, or one acid with some organic acid (acetic, citric, formic, etc.). Precipitation can be effected (though slowly) in H_2SO_4 solution; the smaller the proportion of free H_2SO_4 , the more complete the separation. NH_4Cl favors its separation in a granular form, and checks a tendency to run through the filter paper, which it sometimes exhibits, especially when the solution contains free ammonia. Oxidizes slowly on exposure to the air.

Cond.—Solution should be alkaline or acid only with some of the weaker organic acids. Free mineral acids prevent the precipitation to a greater or less extent. H_2SO_4 has the least effect, HCl the greatest. Boiling facilitates the formation of the precipitate, but increases the solvent power of acids upon it. Fe should be absent.

Sol.—Dissolved by dilute HCl and HNO_3 , or by moderately strong H_2SO_4 when hot. Insoluble in alkalies, neutral solutions

and in organic acids through the latter, when in excess, retard somewhat its formation. Free ammonia has a similar effect.

Contam.—MnS or Ni, Co and Fe sulphides. Fe should be separated previously. From the others it may be freed by resolution, neutralizing and reprecipitating.



Rem.—Na₂CO₃ usual precipitant. When precipitated cold, white and flocculent—by boiling becomes granular and assumes a light brownish shade, probably from oxidation.

Cond.—Solution should not contain bicarbonates or ammonia salts. If CO₂ is evolved by the addition of the precipitant to an acid solution, it must be boiled out. Solution must be rendered alkaline by the reagent.

Sol.—Dissolved by dilute acids, bicarbonates, ammonia salts and solutions containing citrates, tartrates, sugar, etc. Also by solutions containing large amounts of fixed alkaline salts.

Contam.—Alkaline carbonate requiring several washings (by decantation) with boiling water to remove it. Fe₂O₃,—removed by repeated solution in HCl and reprecipitation with ammonia after igniting the precipitate.

SiO₂ by dissolving the ignited precipitate in acid and filtering off.

Ign.—In contact with air gives black Mn₂O₃ non-volatile. Recent investigations tend to show that the composition is not absolutely constant. If alkali has not been washed out, ignition in contact with the air affords alkaline manganate.



Rem.—Usual precipitant, NaNH₄HPO₄ or Na₂HPO₄ in presence of ammonium salts. Best managed by adding the reagent to the acid solution of Mn, boiling and then adding ammonia little by little to the boiling solution, until a slight excess is present, then heating on the water-bath until the precipitate assumes *completely* the crystalline form.

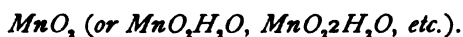
Cond.—The Mn must be entirely in manganous form, and solution alkaline, though not strongly so. An excess of phosphate (about three times as much as is required to form the combination)

must be present. Oxalates should be absent, as well as excessive amounts of ammonia salts or free ammonia.

Sol.—Dissolved by acids. Somewhat soluble in decided excess of ammonia, in NH_4Cl and some other ammonium salts. The solubility in these last is neutralized by the presence of an excess of the precipitant. When too large proportion of ammonia is present, the precipitate, which should be white or faintly pinkish, becomes deeper in color, sometimes quite brown.

Contam.—Practically none if bases forming insoluble phosphates are absent and moderate care is used in washing.

Ign.—Converted to $\text{Mn}_2\text{P}_2\text{O}_7$. The temperature should not be too rapidly raised or there may be some loss. The peculiar nacreous lustre of the precipitate is more pronounced after ignition. Sinters somewhat. Not volatile.



Rem.—For separation in two separate cases. 1. From acetate solution by addition of an oxidizing agent, usually Br. 2. From a boiling solution in nitric acid, by addition of crystals of KClO_3 . Also (3) obtained in titration by the Volhard method—adding standard (volumetric) solution of $\text{K}_2\text{Mn}_2\text{O}_8$ to a solution neutralized by ZnO . In all cases the precipitate probably contains some water of constitution (hydrated oxide).

Cond.—Absence of HCl or other halogen acids, lower oxides of nitrogen or reducing agents. In case 1 a fair proportion of alkaline acetate must be present, to supply base to the mineral acid which might otherwise be set free. Boiling solution necessary.

Sol.—Dissolved or prevented from forming by dilute mineral acids, particularly HCl . Insoluble in moderately strong acetic or in concentrated nitric. When formed it is soluble in strong HCl , forming temporarily an olive-green solution of Mn_2Cl_2 , which becomes practically colorless MnCl_2 by heating. Readily dissolved by HCl or H_2SO_4 in presence of reducing agents (SO_2 , $\text{H}_2\text{C}_2\text{O}_4$, FeSO_4 , etc.).

Contam.—Salts of fixed alkalis, Fe_2O_3 , ZnO .



Rem.—Requires a stronger current than Cu —two or three Bunsen cells (12 to 14 cc. oxyhydrogen gas per minute). The rapid

deposition of the metal is somewhat checked as soon as a coating of nickel has formed, tending to be slower, the thicker the coating. This peculiarity is most marked in cold solutions. In preparing for weighing it is treated as electrolyzed Cu, by washing with water, then with alcohol, and drying at a gentle heat.

Cond.—Solution should contain no other metals of the $(\text{NH}_4)_2\text{S}$ or H_2S groups. Chlorides should be preferably absent. The solution should contain the nickel as double ammonium nitrate, sulphate or oxalate (the latter most advantageous) and excess of ammonia. The operation is more rapid at 70°C . In consequence, ammonia requires to be added from time to time.

Sol.—Dissolves readily in HNO_3 , especially with the aid of heat. Slowly soluble in strong solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

Contam.—Co, Fe and Zn, being precipitated from oxalate solution under the same or similar conditions, may be present in the coat unless previously separated.



Rem.—Usual precipitant, KOH or NaOH. If the solution contains free halogens, or hypochlorites, hypobromites, etc., $\text{Ni}_3(\text{OH})_8$ may be precipitated *black*. The most marked characteristic of the precipitate is the persistency with which it takes up and retains impurities derived from the solution.

Cond.—No bases other than fixed alkalies should be present.

Sol.—Dissolved readily by mineral acids. Soluble or prevented from precipitation by NH_4 salts and tartrates, citrates, etc., or other organic solutions.

Contam.—Alkali used as the precipitant, Fe_2O_3 , Al_2O_3 and silica from the reagents. The precipitate requires thorough washing by decantation with boiling water. After ignition and weighing, it should be dissolved in HCl, which leaves SiO_2 and Al_2O_3 . From this solution the iron should be precipitated by ammonia, filtered, redissolved and reprecipitated again, and these impurities ignited, weighed and the weight deducted.

Ign.—If only moderately, some Ni_3O_4 is contained in the precipitate. If strongly ignited it all becomes *green* NiO . The tint is not a pure green like that of ignited Cr_2O_3 , but lighter and somewhat muddy.

NiS.H₂O.

Rem.—For separation only. Usual precipitant H₂S in weak acetic solution, or (NH₄)₂S followed by acetic acid in excess. Oxidizes easily in contact with the air, with partial formation of NiSO₄. Should be washed by and kept in contact with H₂S water during manipulation.

Cond.—Absence of other members of (NH₄)₂S or H₂S group. NH₄Cl in the solution assists materially its separation in the granular form. Free ammonia, on the other hand, tends to keep the precipitate suspended in the liquid. The solution should be only slightly acid with acetic acid or else barely alkaline.

Sol.—Formation of the precipitate prevented by moderate amounts of free acetic acid or mineral acids. When once formed, it is insoluble in these menstrua unless oxidized by exposure to air, which may easily occur. Somewhat soluble in (NH₄)₂S. To meet these peculiarities of the compound, the solution should be rendered alkaline with ammonia, and H₂S passed in, or (NH₄)₂S added, and when the precipitate is *fully formed*, the solution is acidified with acetic acid, and the precipitate allowed to settle (which occurs readily if NH₄Cl is present). Soluble in hot HNO₃ or in aqua regia. Soluble in KCy.

Contam.—Sulphides of (NH₄)₂S group, if not previously separated.

Ign.—Gives mixture of oxide and sulphate.

Co₂(NO₂)₆KNO₃.

Rem.—Usual precipitant, KNO₃ in a solution slightly acid with acetic acid. Yellow crystalline precipitate, forming best in a warm solution.

Cond.—Solution should contain only Co, Ni and K salts. It should be a nearly saturated solution of KC₂H₃O₆, containing but little free acetic acid.

Sol.—Dissolved by H₂O, acids, NH₄ salts, NaCl and most other Na salts. Insoluble in KC₂H₃O₆ and other K salts. Insoluble in dilute acetic, and in alcohol. The precipitate should be first washed with a 10 per cent. solution of KC₂H₃O₆, and the latter salt finally removed by washing with alcohol.

Contam.—If Ca or other alkaline earths are present, a yellow NiCa nitrite, similar in properties (solubility, etc.) to the Co com-

pound will separate. Pb also gives a similar compound. Care in washing off K salts is necessary.

Ign.—By addition of H_2SO_4 and ignition, the precipitate is converted to $3K_2SO_4 + 2CoSO_4$. One method of management consists in dissolving the washed precipitate through the filter with a little hot dilute H_2SO_4 into a weighed capsule, evaporating and igniting. Some $KHSO_4$ may remain after ignition; removed by addition of a small lump of solid ammonium carbonate and igniting.

CoS.H₂O.

Rem.—For separation only. Properties essentially the same as those of $NiS.H_2O$. Precipitant, H_2S in weak acetic solution or $(NH_4)_2S$. Oxidizes readily in the air when moist, some sulphate being formed. Should be kept in contact with H_2S water during filtration.

Cond.—Absence of other members of $(NH_4)_2S$ or H_2S group. NH_4Cl assists the separation. Unlike $NiS.H_2O$, free NH_4OH does not materially influence the separation. Solution should be preferably *slightly* acid with acetic before filtration (*vid.* $NiS.H_2O$).

Sol.—Formation of the precipitate prevented by moderate amounts of free acetic or mineral acids. When once formed, however, it is insoluble in these menstrua. Of the ordinary mineral acids, HCl has the strongest preventive effect, H_2SO_4 the least; but a very small amount of free H_2SO_4 retards the separation markedly. Soluble in hot HNO_3 or in aqua regia; also in KCy .

Contam.—Usually accompanied by Ni or other members of the group if not previously separated.

Ign.—Affords mixture of oxide (Co_3O_4) and sulphate.

Cu.

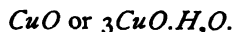
Rem.—Obtained by electrolytic deposition on platinum from acid solution. Free HNO_3 gives a bright coating. Too strong a current gives a spongy, imperfectly adherent coat.

Cond.—Sulphuric acid solution preferable, with or without a few drops of nitric acid. Not over 8 per cent. of free acid should be present. Chlorides disadvantageous. Organic acids (as citric, etc.) should not be present, since they afford a brittle deposit containing organic elements.

Sol.—Easily soluble in HNO_3 . When that acid is present at the end of the operation, flood out the dish with water before breaking the current. Deposit dissolved or prevented from forming by Cl , lower oxides of nitrogen or too strong acid.

Contam.—If free HNO_3 is absent, As, Sb or Bi may occur in the deposit, rendering it blackish. A black coloration is, however, sometimes due to other causes. If free HNO_3 is present, Zn if present, begins to deposit (imperfectly) as soon as all the Cu is precipitated. Pb and Mn may separate from the solution on the other pole, as PbO_2 or MnO_2 , and in case a dish is used these oxides may fall to the bottom and be caught in the deposit. $\text{SnO}_2(x\text{H}_2\text{O})$ may also separate from the solution and be caught in the deposit in the same way.

Ign.—Easily oxidized by heating in air or oxygen. After deposition and washing with water, the water should be rinsed off with alcohol, the alcohol drained off and the dish dried at a temperature which can be borne by the hand, not higher.



Rem.—Usual precipitant, KOH or NaOH in a boiling solution or one subsequently boiled. Na_2CO_3 or K_2CO_3 may also be used in the same manner. The precipitate, at first the light bluish hydrate or basic carbonate, becomes black on boiling from elimination of H_2O .

Cond.—Alkaline solution, not containing bases, the hydrates of which are more or less insoluble. NH_4 salts and organic substances should be absent.

Sol.—Dissolved by acids, also by NH_4 salts and organic solutions, as citrates, etc. Precipitation prevented by alkaline bicarbonates, especially by KHCO_3 .

Contam.—Chiefly the alkali of the precipitant, which is washed out with great difficulty. Some SiO_2 dissolved by the reagent from the bottle in which it was kept, or otherwise introduced, may also be present. Left behind on dissolving in acid the ignited and weighed precipitate.

Ign.—Obtained as black CuO . Some reduction to the metallic form by contact of C may occur but as the metal is not volatile it is readily restored by ignition with a few drops of HNO_3 . The

use of platinum where reducing substances may be mingled with the precipitate is inexpedient. Precipitate quite hygroscopic after ignition.

CuS.

Rem.—Usually for separation. When for determination, treated as suggested under "*Ign.*" for production of Cu_2S . Has ordinarily a brown to black color, but when precipitated along with sulphur has an orange-red color.

Cond.—Acid solution usually used, though not indispensable. Precipitation can be effected promptly in presence of moderately strong H_2SO_4 or of HCl if not too strong or hot. If HNO_3 is present, the solution must be dilute and cold.

Sol.—Soluble in hot dilute HNO_3 and in HCl when hot and moderately strong. Somewhat soluble in $(\text{NH}_4)_2\text{S}$, especially if polysulphides are present. Insoluble in HCl or H_2SO_4 , or in NaHS or KHS , unless polysulphides are present.

Ign.—Partly reduced to Cu with C . Converted to Cu_2S by mixing with sulphur and igniting in a current of hydrogen (in a Rose crucible).

[TO BE CONTINUED.]

NOTE ON FILTERING CARBON SPONGE FOR COMBUSTION.

BY W. P. BARBA.

It will have been noticed by every chemist using the double copper salt for dissolving steels for combustion, that there is often great difficulty in filtering and washing the sponge; especially in steels which have been treated by forging, oil tempering and annealing, the sponge forming a sticky, gummy mass, which immediately clogs up the filter, often requiring an hour or more to filter and wash.

I have found that this can be remedied by letting stand 10 to 15 minutes for settling, as usual, then decant on the asbestos filter, the clear liquid, until most of it is poured on; then pour into the beaker a few cc. of the suspended asbestos (same as is used in making the filter), taking care not to add so much as will fill up the boat; a very little suffices; after which proceed as usual.

This keeps apart the particles of carbon sponge and allows of

very rapid washing. In fact, the filter will allow wash water to pass through as rapidly as it can be poured on. It is best to use only a slight vacuum and pour on from a beaker.

That the washing is thorough, I have proved by experiment. It is obvious that this may be used in many instances on the Gooch crucible.

LABORATORY OF
THE MIDVALE STEEL COMPANY,
NICETOWN, PHILA.

THE DETECTION OF ARSENIC.

That arsenic may be precipitated from its solution in hydrochloric acid by hypophosphorus acid has been known for some time. If to the solution in hydrochloric acid potassium iodide is added, and then hypophosphorus acid, the test is a much more sensitive one, the arsenic precipitating as a brown to brownish-black powder. In this way it is possible to detect .025 mgm. arsenic trioxide dissolved in 10 cc. of the solvent. So far as the delicacy of the test is concerned, it is a matter of indifference whether the arsenic is present as arsenious or arsenic acid. The test is inapplicable in presence of the noble metals and copper. Antimony and bismuth are precipitated only from concentrated solutions, and the precipitation is incomplete. The precipitates are also of a different color, being black. If it is suspected that antimony or bismuth may be present, the precipitate is filtered through a small filter and dissolved, without previous washing, in a solution of bromine in hydrochloric acid. The arsenic is then reprecipitated in the same way. In presence of antimony and bismuth, it is best to omit adding potassium iodide. In presence of iron in large amount, the air should be excluded during the test, as otherwise the yellow color of the ferric chloride formed might lead to an erroneous conclusion. This method of separating arsenic from antimony and tin cannot be used quantitatively because the precipitate oxidizes readily and cannot be washed without oxidation.

When iron is placed in a hydrochloric acid solution of arsenic and antimony, the antimony is completely precipitated, and the arsenic goes off as arsine. In order that traces of arsenic may be detected in this way, the iron must be entirely free from sulphur.

Sulphur-free iron for this purpose may be prepared as follows : To a solution of 200 gms. commercial anhydrous ferrous chloride in 500 cc. water, some pure iron from a previous preparation is added to precipitate any more electro negative metals present, and then barium chloride to throw down sulphuric acid, which is also present. 25 cc. glacial acetic acid is added to the filtered solution through which the current from a Bunsen cell is passed. The negative electrode is a platinum foil, while the positive is a piece of the purest iron obtainable. With 100 sq. cm. electrode surface, 2 gms. of iron per hour may be thus deposited. The iron may be stripped from the platinum easily. It is very brittle, and oxidizes readily. It is washed quickly with water, alcohol, and ether, and dried in a vacuum over sulphuric acid, and kept in a desiccator. In using this iron in the Marsh apparatus, hydrochloric acid is the best solvent, and the gas given off is led through a 10 cm. layer of wadding contained in a tube. When pure antimony solution is used, no mirror is obtained, but by the addition of a very small amount of arsenic a mirror is obtained. With iron, only about 10 per cent. of the arsenic is converted into arsine, the rest separating as metallic arsenic. With zinc, 94 per cent. is converted into arsenic. In presence of antimony chloride, however, a much larger quantity of the arsenic is converted into arsine by the iron, since, working in this way, .015 mgm. of arsenic could readily be detected in 2 hours. With iron alone, the test is not as good as desirable, since less than .1 to .15 mgm. arsenic could not be detected. At the best, the test is less delicate than with zinc.

When platinized zinc is used in the Marsh apparatus, the test is less sensitive than with pure zinc alone (Joh. Thiele, *Ann. der Chem.* 265, 55).

E. H.

COLORIMETRIC METHOD FOR ESTIMATING GALLO-TANNIC ACID, GALLIC ACID AND TANNIC ACID.

0.4 gm. potassium ferricyanide are dissolved in 500 cc. water and 1.5 cc. liquor ferri chloridi are added. This is called the "iron mixture."

0.4 gm. of dry gallotanic acid, dissolved in 500 cc. of water, and 50 cc. of this made up to 500 cc. with water constitutes the

"tannin solution." An infusion of oak bark is made by exhausting 8 gms of the bark, making up the infusion to 500 cc. with water. Six two-ounce clear glass tumblers are placed on a white surface. 5 drops of the infusion of bark is dropped into one with a pipette, and, in the others, with the same pipette after carefully rinsing, 4, 5, 6, 7 and 8 drops of the tannin solution, 5 cc. of the "iron mixture" are added to each, and in about one minute, 20 cc. of water, and within three minutes, the shades of color are observed. The number of drops of tannin solution used, indicates per cent. of gallotannic acid in the bark. The reagents used, viz., the "iron mixture," tannin solution, and infusion must be freshly prepared and must not be exposed to the rays of the sun. In case of substances containing more than ten per cent. of gallotannic acid, for which the above is written, the infusion is first diluted with an equal quantity of water, so that the color may not be too deep a blue. The gallotannic acid having been estimated, the gallic acid is determined as follows: Precipitate the tannin from 50 cc. of the infusion, (= .8 gms. bark) with 0.2 gms. alum and 20 cc. of a solution of gelatin (3 gms. to 1 liter.) mix well, make up to 250 cc. with water, filter off a little of it. Put five drops of the filtrate in the first glass, and proceed according to the method as above described, using a solution of 0.02 gm. pure dry gallic acid in 1 liter, of water, instead of the "tannin solution." To make this solution, dissolve, 2 gms. of gallic acid in 500 cc., and make 50 cc. up to a liter water, one eighth of the number of drops of the gallic acid, used to produce the same shade of color as is caused in the glass containing the filtrate, will give the per cent. of gallic acid in the bark, which deducted from the gallotannic acid, will show the per cent. of tannin present.—*Samuel J. Hinsdale, Chem. News* 64, 51.

A. H. W.

NEW METHOD FOR THE SEPARATION OF IRON, ALUMINUM AND CHROMIUM.

To the sulphuric acid solution of the oxides is added sodium carbonate until a small permanent precipitate is formed. This is just dissolved by adding dilute hydrochloric or sulphuric acid, after which the solution is well stirred. Thoroughly washed, freshly

precipitated manganese dioxide, formed by adding together manganese sulphate and permanganate of potassium solutions in molecular volumes, is then added in slight excess, according to the amount of Mn and chromium contained in the solution. It is, perhaps, advisable to test the solution after having been kept at the boiling temperature for about ten minutes, with ferrocyanide, to find if all the iron has been precipitated. If not, more manganese dioxide must be added, and the solution again boiled. After being filtered, the filtrate will contain all the aluminum and the chromium or chromic acid if the quantity of manganese dioxide added was sufficient to thoroughly oxidize it; also the small amount of manganese that has been dissolved.

The precipitate contains the excess of manganese dioxide and the oxide of iron. The iron may be dissolved and titrated, or separated from the manganese by the acetate method.

The filtrate is made ammoniacal and boiled, the alumina filtered off, and the chromium, after reduction, precipitated from the filtrate with ammonia.—*C. Marchal & J. Wiernik, Ztschr. angew. Chem., 1891, 511.* J. E. W.

THE QUANTITATIVE ESTIMATION OF BROMINE AND IODINE BY CHLORINE.

Bromine and iodine are precipitated as the silver salts and weighed, after which they are converted into chloride by a stream of chlorine gas, or as the author advises, a stream of hydrochloric acid gas.

The conversion is not so complete for the iodine as for the bromine.

For from 0.1 to 0.4 gm. of AgBr the gas must be allowed to pass over it for at least one hour if hydrochloric acid gas is used, but with chlorine, five minutes for bromide and ten for iodide is considered sufficient.—*E. Nihoul, Ztschr. angew. Chem. 1891, 441.*

J. E. W.

— THE —

Journal of Analytical AND Applied Chemistry.

PYRITES AS A MATERIAL FOR THE MANUFACTURE OF SULPHURIC ACID.

BY WM. H. ADAMS, M.E.

No subject before technical writers has greater interest to the general public, at the present time, than the manufacture of sulphuric acid—the basis chemical of all civilized communities—an industry which is developing and expanding throughout the country in a ratio beyond parallel in any branch of chemistry.

In the year 1865 less than 40,000 tons of this acid was manufactured in America, notwithstanding the stimulated consumption due entirely to war demands. In 1870 it had risen to about 70,000 tons; in 1875 to nearly 100,000 tons; in 1880 to over 285,000 tons; in 1885 nearly 400,000 tons; in 1890 about 510,000 tons; and this year it will be nearly, or quite, 535,000 tons.*

A little over 50 per cent. of the acid thus manufactured in America is used directly in decomposing or dissolving phosphatic rocks, for superphosphates and fertilizers; about 35 per cent. is required for the refining of petroleum, the balance is used for all purposes in the trades.

It would be fair to state the sale price of this tonnage at over \$20,000,000 annually at present, and the cost of the sulphur required for the manufacture may be expressed, in round figures, as \$2,500,000 for brimstone, and \$1,100,000 for pyrites.

For over twenty years past discussions have been going on, and articles have been written for the technical and trade journals, calling attention to the differences in cost of manufacture of this acid when made from brimstone or from pyrites. These articles

*This tonnage is calculated on the basis of commercial acid (66 degrees Beaume), but it will be understood, of course, that as manufactured in chambers, the tonnage is double this amount.

seem to have had very small weight upon the older established enterprises, although tending to the enlightenment of the newer and later class of workers in this field, and while not without their value in a technical sense, yet have not been productive of that good which the subject demanded. It may be said that a scattering fire of this sort cannot be expected to produce the results aimed at, and perhaps too much of the literature has come so directly from those interested in the introduction of pyrites that due weight has not been given the facts as presented. Be that as it may, the problems which were new to chemical manufacturers ten years ago have been practically demonstrated since that time by another class of workers, whose interests lay more particularly in the direction of copper smelting as a secondary process, and we now have all the necessary economic data to bring to bear, with the technical work as well, so that a compilation of actual practice in this field cannot but be acceptable to the general reader.

When we say that pyrites is the cheaper source of sulphur for the manufacture of sulphuric acid, it is because the following statement is accepted as substantially correct :

One ton of brimstone "seconds" cost to average ex-ship, at any of the Atlantic ports	\$25
This ton of brimstone will net 95 units of pure sulphur, after losses of handling, storage, burning, and escape of gas are allowed for.	
The equivalent of above, 95 units of sulphur, can be sup- plied from pyrites (two and one-half tons), and laid down at any of the seaboard factories at an average cost of	13
The difference in cost of equal amounts of sulphur, at fac- tory and in manufacture, is	\$12

There are some costs inseparable from the use of pyrites which are not incurred when brimstone is used, but in the large way the cost of burning the ores by mechanical means does not materially exceed the cost of burning brimstone, and it is entirely safe to say that under all circumstances, where the construction of works is modern, there will be a saving of at least \$10 per ton of sulphur consumed.

This statement is sufficiently startling to warrant bringing together all the facts which shall tend to make this subject clear. It goes without saying that busy workers in chemicals, whose

fortunes have been made during the last ten years of extraordinary development in this industry, have not accepted these figures, or we should have a different story to tell as to opening of mines, and a smaller importation of brimstone to record. It may be reasonable that manufacturers of acids, *per se*, should subordinate this special industry, wherein there has always been the liveliest competition, to other and supposably more profitable branches of business, and it is not difficult to understand that owners of works established twenty to thirty years past, whose location is now in well built-up portions of our cities, might not wish to change from brimstone to pyrites, as the questions arising out of the handling and storage of the bulky ores, etc., and the proper disposition of the cinders, etc., would open up problems which the savings on a small manufacture would hardly counterbalance.

We can understand that to such works the small savings would be no object, but what can we say of the newer and more favorably located works, numbers of which have been erected during the past five years under every favorable condition, and yet built to burn brimstone? A state of affairs which continues to hold us in bondage to producers of brimstone in Sicily, and other foreign countries, compelling the payment of large sums of money annually for products which can well be supplied from our own soil, causes the greatest surprise and considerable speculation among the foreigners themselves, inasmuch as we are usually prompt to take advantage of our own resources.

93 per cent. of all the sulphuric acid made in Europe is made from pyrites, and it is a fact that old-world practice with ores, whether high grade sulphur ores from Spain, Norway, etc., or more complex products, which result from the mining and concentration of ores of gold and silver, is as intelligently understood and successfully carried out, for the large manufacture of acids, as is our practice with the brimstone plants.

We have several works in this country at present, with a daily consumption of 25 to 75 tons pyrites, and while the practice in such works is substantially the same as in foreign examples, there are modifications which lessen the costs of manufacture to us.*

I could cite two works whose acid cost-sheet would show better

*Trans. Am. Inst. Min. Eng., 18, 496.

than the best of foreign works—this notwithstanding the higher prices paid for nearly every item of materials purchased, labor, etc.

Why is it, therefore, with opportunities given our students to master old-world practice, and with the general knowledge promulgated constantly by men of liberal culture, that we are not to-day in this country utilizing the untold wealth which lies at our doors, though hidden? With the proverbial aptitude credited to Americans, we should long ago have brought back a thousand of our brightest students to occupy this field alone; our junior partners, imbued and saturated with the methodical systems of the European metallurgical centers, expanding, improving and perfecting the problems of this nature so backward in our land.

Other branches of metallurgy encourage and foster this principle, and the whole world stand in admiration of successes gained by us in nearly every field except chemistry.

We might cite, for example, the failure of the operations which were inaugurated in Atlanta, Ga., in 1882-84, where for the first time in local history an attempt was made to utilize pyrites for acids, and the cinders or residues thereafter for the manufacture of copper, in ingots. It is a difficult matter to understand why failure should have been written in that case, and that for more than six years the problem should have remained unsolved by a trade demanding so large quantities of acids for the manufacture of fertilizing products. The principle involved is one of the simplest before students of the old world, which has also been before us and solved successfully for the past twenty years, the process now being carried on in a very large way by works near New York utilizing the ores from the Canadian mines.

These Canadian ores are almost identical with the ores from Tallapoosa and Dallas, in Georgia, Ore Knob, in North Carolina, Louisa County, Va., etc., and have been shipped to the United States for the manufacture of acids and copper regularly since the year 1867, being worked at the present time at the rate of 250 tons daily, every step of the process fully understood, even to the extraction of silver and gold from the "regulus."

If we compare the working statements of the two examples cited (an average statement covering the past ten years), the results will be sufficiently striking to warrant the foregoing remarks.

STATEMENT OF WORKING RESULTS IN ATLANTA, GA.

Capacity of Works, 300 tons Pyrites monthly, equal to 100 tons Brimstone.

Production.

300 tons pyrites ores will produce 450 tons chamber acid (50° B.), average selling price, \$14	\$6,300.00
300 tons pyrites ores, with 5 per cent. copper, will produce 30 tons regulus (45 per cent. copper), average selling price in Baltimore, net, \$83	2,490.00
Total receipts for the month	\$8,790.00

Manufacturing Costs.

300 tons pyrites ores (38 per cent. sulphur, 5 per cent. copper), delivered at factory in Atlanta, average cost at works, \$8	2,400.00
All acid manufacturing costs, crushing, burning, storage, etc., \$5	1,500.00
Smelting charges to produce 30 tons regulus, or, 300 tons smelted at \$2 per ton	600.00
Total costs of the factory each month	4,500.00
Balance is monthly profit	\$4,290.00
Or, per ton of mine ores used, \$14.30	

STATEMENT OF WORKING RESULTS IN NEW YORK CITY.

Capacity of Works, 300 tons Pyrites monthly, equal to 100 tons Brimstone.

Production.

300 tons pyrites ores will produce 450 tons chamber acid (50° B.), average selling price, \$8	\$3,600.00
300 tons pyrites ores, containing 5 per cent. copper, will produce 30 tons regulus (45 per cent. copper), average selling price, net, \$90	2,700.00
Total receipts for the month	\$6,300.00

Manufacturing Costs.

300 tons pyrites ores, 38 per cent. sulphur, 5 per cent. copper, delivered at factory near New York, average cost, \$7	2,100.00
All acid manufacturing costs, crushing, burning, storage, etc., \$5	1,500.00
Smelting costs to produce 30 tons regulus, or, 300 tons smelted at \$1.50	450.00
Total monthly costs	4,050.00
Balance is monthly profit	\$2,250.00
Or, per ton of mine ore used, \$7.50 profit.*	

*In the above calculation I assume that the mine and works are owned by the same parties, or worked in common. If the mines belong to separate owners, the cost of ores should be increased to correspond with market prices from time to time.

These figures are based upon actual workings of to-day, that is, an average which will cover all contingencies for the past ten years, and as emphasizing the point made in my foregoing remarks, it may be stated that during the period named, the cost of brimstone in the city of Atlanta has averaged not less than \$26 per ton, while ores could have been obtained which would have supplied the same amount of sulphur at a rate of not to exceed \$14 per ton.

Some writer has said, "It is obviously unfair to make any allowances for shortcomings which have no right to exist, although it is the duty of teachers to show to those who, from ignorance or obstinacy, still cling to old ideas and methods, what is actually being done by new men and new means."

To elaborate this point, a bit of history coming under my own observation, may be inserted here :

A very complete works for the manufacture of acids of all kinds was erected in 1869-'70, the location being in the centre of a cotton and wool district. Pyrites was chosen as the source of sulphur.

Operations were begun with men brought from England ; with ores unknown as to quality or quantity ; competing with established works using brimstone whose owners were financially interested in the mills to be supplied with acid. Handicapped in almost every way by local prejudice and ignorance, it need not be said that the trials and losses of the first year were many and severe. Primarily it seemed an impossibility to produce acid from the pyrites mined in Canada, Maine and Vermont, but as a last effort the trained workers from Canada came to the assistance of the English workmen to save the reputation of the process. When success was won in manufacture, new troubles arose from reported poisonous qualities of the acids ; their destructive properties as solvents ; or, for dyes and precipitants, etc. ; until with the worst of management in the factory, and bitterest opposition outside, the works, costing about \$150,000, came to the hammer, and were sold at a ridiculously low price to one of the most determined of opponents. After remodeling by expert talent, these works started successfully from the first hour, are at present running with a consumption of probably 35 tons daily of pyrites, with the same ores declared useless ; supplying the same customers who once

were unable to use the poisonous stuff, and the present owners are still advising new-comers against the use of pyrites with such success that but two factories have as yet been erected in that territory to compete with the beginner.

The disappointments and losses, incident to a proper education of our people during the early years of pyrites working, are freely quoted to deter manufacturers from now entering the field, and facts showing the real benefits to be derived from a practical manipulation of ores at this period, after our long experience, are difficult to obtain, although the constant increase in pyrites plants by the stronger companies surely indicate the satisfactory nature of the business.

It may be excusable in an old established works, located, as stated, in the midst of a thriving city, and with a plant obsolete in construction and materials, that radical changes and improvements are not made to accord with the use of ores, but it is incomprehensible why new works, built upon supposed modern lines, on virgin ground, and handicapped with none of the obsolete ideas, should deliberately choose brimstone burning, with fluctuating markets and uncertain supplies, always at double the cost of pyrites ores.

It is not true of any other industry we can name, and, in fact, it may be said that no other industry would be supported which had not for its basis some more certain assurance than has been the price of brimstone for twenty years past. It can be stated in a forcible manner that no factory for the manufacture of brimstone acid exclusively has been able to exist during the past eight years.

All the factories formerly known as acid works, have turned their acids into other products, in order to keep in the trade, while many of them have been torn down, unable to retain their positions.

Of the newer factories, the greatest increase has been for the manufacture of sulphuric acid to be used exclusively for fertilizers. This class of business was for a long time dependent upon the supplies purchased from chemical works, but as trade increased, it became absolutely necessary that they should free themselves from dependence upon outsiders, so works were erected on their

own lands in the cheapest possible manner, with the least regard to the latest ideas governing construction, and with no regard to the future of such a business. Except for thoughtless methods of construction, it is impossible for us to understand why so many of the works were located in their present positions, and time will more and more demonstrate the lack of wisdom which prompted such steps.

Brimstone, beyond all other substances essential for the manufacture of sulphuric acid, is subject to wide fluctuations in price, by reason of irregular manufacture, varying freight rates, war tributes, etc.

The following table will sufficiently prove this statement.

Table showing Tonnage of Brimstone imported into the United States and Canada, from 1876 to 1891.

	Tons of 2000 lbs.	Total Values.	Average Price per Ton.
1876	48,966	\$1,473,678	\$31.00
1877	43,444	1,242,788	28.60
1878	47,922	1,173,156	24.50
1879	65,919	1,487,698	22.60
1880	83,236	1,927,502	23.15
1881	105,438	2,713,494	25.73
1882	97,956	2,627,402	26.82
1883	94,536	2,288,795	24.20
1884	105,143	2,242,678	21.33
1885	96,844	1,941,943	20.00
1886	117,396	2,237,332	19.00
1887	97,383	1,688,360	17.33
1888	99,253	1,581,582	15.94
1889	130,191	2,025,644	15.55
1890	123,000	2,030,700	17.00 (partly estimated)
1891	121,000	3,146,000	26.00

To clearly understand present and future values of ores for the manufacture of sulphuric acid in this country, it is proposed to present data covering the source, cost, etc., of both brimstone and pyrites, so that a clear understanding of the peculiar trade positions of each may be gained.

Brimstone is the commercial name for sulphur procured by several processes of manufacture starting from a base, or original product of sulphur, in sedimentary rocks or from natural formations. Thus, brimstone is derived from earthy materials which

contain sulphur; but it cannot be called brimstone if deposited from solutions.

Sulphur in various forms and in varying conditions is found widely distributed over the earth's surface, and nowhere in greater quantities and within easier reach than in our own land.

Alaska, Utah, Nevada, Louisiana, Mexico, Central America, Brazil and other South American countries have the most extensive deposits.

It has also been found in France, Spain, Russia, Poland, Austria, Eastern Egypt, the Grecian Archipelago, Northern and Southern Italy, and largely in Asia,—Japan having already been a seller in our markets.*

We rarely hear of any of the sources of supply mentioned above, except Sicily, although they are coming into notice from year to year. Thus Japan has produced inferior brimstone for the past six years, the article being used mostly by works on the Pacific coast of the United States. It is owing to the many difficulties of the inceptive workings in regions remote from supplies, which has produced such poor results to date, but if the problem of freights can be solved in some way, there will be an enormous output from that country, at prices even lower than those possible from Sicily.

The export trade is handled entirely from Hakodate, the refined brimstone coming from the south-east side of the island on which Hakodate is situated (Atosanobori mines near Kushiro), being the product of the soil which lies on the slope of an extinct volcano.

It is fairly estimated that 2,000,000 tons of brimstone will be taken from this deposit at a cost of not to exceed \$8 per ton on board at Kushiro, and mining operations at present will enable the shipment of 15,000 tons annually. The freights to Hakodate are \$2 per ton, thus making the actual cost, at present, \$10 per ton on board ocean vessels bound for markets.

The question of working any of these deposits of sulphur is purely one of marketing the products—distance from points of consumption and transportation being the main factors. Thus in Utah and Nevada very pure deposits exist which would supply our needs for centuries.* Unfortunately there is no demand for quan-

*Trans. Am. Inst. Min. Eng., 16, 33.

tities in that section, or in sections which can be reached from those mines, transportation to the eastern and western markets exceeding the cost of foreign brimstone at our seaport cities.

This may be said to cover the condition of affairs with reference to all the other deposits mentioned. The deposits on the Island of Sicily, in the Mediterranean sea, are, however, so favorably located for production and distribution to the principal consumers of the world as to give them the virtual control of the trade.

For over 300 years these deposits have been worked and studied, although the really large output of sulphur has been since 1820.

The sulphur found on this Island is of two kinds, one of which is closely allied to sedimentary rocks, and the other from volcanic emanations. It is generally believed that Mt. Etna, situated in the east, is responsible for these deposits, but scientists do not accept this theory of late years, offering several other explanations of the varying conditions which large workings have disclosed, (*a*) emanations of sulphur vapor expelled from metallic matter existing in the earth, (*b*) sulphuretted hydrogen (from the union of sulphur vapor and steam) passing through fissures of stratified rocks, (*c*) sulphuretted hydrogen from the decomposition of calcium sulphate in the presence of organic matter, (*d*) the action of seawater upon animal remains, etc. At the Government school in the neighborhood of Caltanissetta, are shown many specimens of interest in connection with these deposits, such as geological sections of the principal mine locations, specimens of fish, eggs, insects, etc., found in the strata, which consist of rock-salt, marl, bitumen, etc., underlying the sulphur.

About 250 mines are at present working, the number lessening every year, and the tendency being to concentrate the mine properties in strong hands, with reduction of costs in every department.

All details of cost of production, taxes, etc., are constantly being presented through our consular agents, and as it is generally admitted that the selling price in American ports is as low as it can possibly be made with existing methods of manufacture, we may assume, without the necessity of presenting facts and figures, that except for commercial depressions, compelling the unloading of

stocks by the strong companies now in control, that prices for brimstone "seconds" and "thirds" will not vary from prices we have lately been paying, as shown by the table already given.

These facts are necessary to be clearly understood, in order to calculate workings for the future in this country.

There are, however, circumstances which may arise to change completely the channels of trade we are now depending upon, and which may also lessen prices materially.

As likely to effect us in the United States, work has been commenced on the sulphur deposits at Calcasieu, Louisiana.

A French company spent a very large sum of money on this property, during the years 1880 to 1884, and failed to secure a depth of 100 feet in the shaft, although every appliance of modern engineering was utilized, and no expense spared. The small island which emerges from the waste of lagoon and marsh, and under whose surface diamond drill borings have shown such enormous amounts of sulphur-bearing materials, seems to be merely a "hummock" of generous proportions floating on a lake of silt, mud and quicksand, which is saturated with heavy petroleum. The problem is to sink through this treacherous mud until some foundation is reached which will support the proper working shafts, after which the excavation of the stratum, containing more or less sulphur, will be carried on in the ordinary manner. It is estimated that sulphur, equivalent to commercial brimstone, will be obtained at a cost of \$6 to \$8 per ton.

The manufacture of pure sulphur from the waste mud, left in the vats after the lixiviation of black-ash, is an interesting operation which has not been written up, although the details are the basis of many patents, therefore obtainable by all chemists.

The source of this late-day industry lies in the enormous banks of mud, the accumulations of many years. It is no unusual sight to see large buildings erected on the heaps which have been temporarily disposed of, and millions of tons have been wasted and are beyond recovery, having been filled upon marsh lands, or carried out to sea from the lower deposits. On exposure to air, this waste absorbs oxygen so rapidly as to become strongly heated, even red-hot at times, giving off an intolerable odor of sulphur dioxide and sulphuretted hydrogen gases.

Messrs. Chance Brothers have lately made use of a process for recovering sulphur from this waste—the perfected Shaffner and Helbig—which promises to utilize the enormous deposits so lately considered worthless, the annual tonnage now thrown out from the alkali works being 1,500,000 tons in England, and as much more on the Continent, containing at least 400,000 tons pure sulphur.*

This process may be concisely stated as follows :

The waste from the lixiviating vats, in the form of a thick mud, is diluted with water and brought to the consistency of a thick cream by mechanical stirring in large cast-iron cisterns. From thence it is pumped into cast-iron cylinders, 16 feet long and 5 feet in diameter, which are mounted on trunnions and connected in series of the required number. These cylinders stand on end, with the man-holes on the floor of one story and the discharge openings just above the floor of the story below. These cylinders are usually connected in series of seven, and are worked alternately in series.

Carbon dioxide gas (the product of the ordinary lime-kiln process) is forced through the contents of the cylinders, with the result that sulphuretted hydrogen gas is generated, and this gas is transferred to the ordinary gas-holder. It is obvious that operations on a practical scale demand the alternate use of each of the cylinders, and that fresh carbon dioxide is passed into the nearly exhausted waste, while the fresh waste is pumped into the cylinder last to receive the gas. Also, that either cylinder can be disconnected for emptying the exhausted waste without interfering with the process. It will be understood that all details of connections, etc., are similar to the well-known plant made use of for the processes of kindred nature.

The resultant gas from this process is taken from the storage holders through a meter, and, with air from a separate holder, passes through a meter, in the ratio of 12 of air to 8 of gas, into a Claus kiln, which is an iron cylinder packed with broken refractory materials, into which the gases enter, circulate, mix, and are finally ignited. The flames from this kiln are passed into a brick chamber, where most of the sulphur is formed, and drops to the floor in a molten state, and from thence to a second chamber,

*J. Soc. Chem. Ind. 1888, 162, 210.

where the cooler gases form flowers of sulphur. In this recovery process there is an escape of gaseous mixture containing variable amounts of SO_2 and H_2S , stated to be from 30 to 50 gms. sulphur per cubic meter, which loss is almost a necessary evil owing to the enormous quantity of foreign gases, chiefly nitrogen.

The product is the sulphur of commerce, which has been seen in large quantities in this country, already, and will soon be an article of commerce generally, as it is substantially pure sulphur, and in every way better than commercial brimstone "firsts."

Over 500,000 tons of this sulphur is produced at present in twenty works, and as England consumes about that amount of pure sulphur for all manufactures, it will be seen that she will soon be independent of all foreign countries.

In one works alone, over four million cubic feet of sulphuretted hydrogen gas are being produced weekly, and taking quantities of the waste mud into account, it will be seen that it is only a matter of time and money when the production of sulphur from this source will be enormous, and seriously affect the world's markets.

If sulphuric acid be a desired commodity, the gas from the holder is mixed with sufficient air to form sulphur dioxide and water vapor, the resultant gas being conducted to the towers and chambers in the usual manner.

We thus have a threatening rival to the worn-out mines of Sicily, and can without any doubt prognosticate the manufacture of pure sulphur from these waste heaps of England and the Continent at prices which can never be equaled by the Sicily mines and works.

The waste used from alkali works averages about $12\frac{1}{2}$ per cent. sulphur, fully as much as the mine ores of Sicily, and if costs of extraction were equal, the saving in freights alone would be sufficient profit.

A German patent of considerable merit has attracted the attention of manufacturers lately, and works have been erected to demonstrate values on a large scale.

The proposition is to obtain sulphur, commercially pure, from the calcium sulphide of alkali waste, by decomposing it to obtain sulphuretted hydrogen, which is then passed over alkaline earths or sulphates of an alkali, strongly heated.

As applicable to our own country (no alkali waste being obtainable) suppose we start with sulphuretted hydrogen, formed in any manner.

This gas is passed over pieces of gypsum packed in pipes or retorts and heated to redness. A reaction takes place by which the oxygen of the sulphate combines with the hydrogen of the gas forming water, while free sulphur is produced, the residue being sulphide of lime. Now if air is passed over this sulphide of lime, the heat being kept up, oxygen is again absorbed, the gypsum is renewed and ready for the reaction of a fresh lot of sulphuretted hydrogen.

The details already given, in working the Chance process, will answer for this process as well.

We thus have before us, at the present time, two propositions worthy of careful study: one a problem of mining under difficulties which have never been surmounted, as yet, and offering from start to finish problems which must be met and overcome by time and large expenditures of money; the other a series of problems in chemistry, aimed to utilize waste materials which are already practically unlimited in supply, and which are being utilized by capital sufficient to command success sooner or later. Success in this case will mean the possibility of supplying the markets of this country at prices which will keep out Sicilian sulphur.

Consumers of sulphur should carefully consider the effect of such a possibility, and the financial bearing on trade, as it is almost certain we shall see the brimstone of Sicily coming in less quantities from this time on.

For arguments sake, suppose that Calcasieu sulphur (equal to present grades of brimstone) were to be offered in quantities within five years from date, how would it affect us at home.

The deposits are of course to be opened by a speculative syndicate whose operations are strictly business-like, and we should not expect them to lower prices to the trade, further than to control all trade in the territory they are able to practically reach. Now when the price is reached at which they expel foreign brimstone, it follows as a natural sequence that such price will rule as a minimum for all time thereafter.

With the known costs of mining, smelting, taxes, shipping and

all other charges against Sicilian brimstone, we may reasonably fix the price at \$17.00, below which price there can be no importations when surplus stocks are worked off. Thus large lots of Calcasieu offered at \$16.00 per ton delivered would command the markets of this country.

One of the effects which follow the exclusion of competing products is the fluctuation in price of an article of so general and yet so uncertain a consumption. With foreign brimstone excluded by any of the causes named, what is to hinder the rise in price of our Calcasieu sulphur. With foreign brimstone there is the matter of freights, which, in case of war in Europe, or other circumstances and causes well known to the trade upsets all calculations.

Are we in any different position in a trade sense, whether the supply is controlled by Calcasieu, Utah, Nevada, or any brimstone producer? Is it not substituting one syndicate for another, and the consumer paying the last dollar the circumstances will warrant?

[TO BE CONTINUED.]

WATER SUPPLY AND PUBLIC HEALTH.*

BY ALLEN HAZEN.

During the last few years there has been accumulating an overwhelming amount of evidence that typhoid fever is often transmitted from one person to another by drinking water. I need not refer to the experience of foreign cities, but only to mention epidemics during the past year alone, at Albany, Wheeling, Duluth, Lowell, and Lawrence, besides many others of less extent. In a part of these cases, at least, most thorough investigations have been made, showing beyond question that the excessive death rates were due to the pollution of the public water supplies.

Investigations have also been made, both in England and in India, showing that Asiatic cholera is most frequently conveyed by drinking water, and we have to consider what part our water supplies might take in its propagation in the unfortunate event of its gaining a foothold on our shores.

It behooves us, then, to give this subject most careful consider-

*Read before the American Public Health Association, Kansas City, Mo., Oct. 20, 1891.

ation, with a view to understand the exact method of transmission, and if possible, to find measures which will secure relief.

Both typhoid fever and cholera are caused by the growth within the body of particular species of bacteria, which are most frequently taken into the system through the mouth, either with the food or drink; and it is the presence of these particular germs in a water which gives it its power of causing disease. A water may be muddy, or hard, or discolored by organic matter; it may even be sewage-polluted and swarming with germs, but if it does not contain the objectionable species, its use will not cause the diseases in question.

At first sight it would appear that bacterial examination for the hurtful forms should give the true criterion of the character of a water. The difficulty of the search for pathogenic organisms, however, has greatly limited this line of work, and only confirmatory results have thus far been obtained. The bacteria have not been found until after their presence has been indirectly proved by an excessive number of cases of typhoid fever among the users of the water, which could not be ascribed to any other cause. Improved methods are being suggested for the detection of the typhoid bacillus, and it is quite probable that in the future we shall have methods at our disposal far more satisfactory than those which we have been using.

But when we have a greatly improved method for the detection of the bacillus, how much will it help us? That the fever is due to water supply has been amply proved in numerous cases, by eliminating other possible causes, and by showing that those who drank from one water supply suffered, while their neighbors, with other water, remained free. Now, when it is once established that a water supply causes typhoid fever, the number of cases among the consumers of the water is a far more satisfactory index of its condition than any laboratory test, however perfect. In the case of proposed water supplies not yet introduced, the death rate test cannot be applied, and we must have recourse to other methods. But, supposing it were possible to show, absolutely, that disease germs were absent from a given river, no proof has been given that they will be absent a month hence under somewhat changed conditions of temperature, volume of water, etc. The

Merrimack river water often produces typhoid fever among those who drink it, but not always. There are times when its influence is scarcely perceptible; at other times it is capable of causing an epidemic. Aside from any analytical imperfections, the bacterial methods cannot guarantee the future of a water from its present condition, and as it is the future in which we are mainly interested, we must look for other sources of information.

So far as we know, the germs of communicable disease are absent from unpolluted waters; they are only introduced by sewage. Waters which are absolutely free from the products of human life are, in general, safe for drinking. It is our first problem, then, to determine whether a water is sewage polluted. This is done by inspection of the water-shed, or by chemical analysis, or both. With surface waters, inspection of the water shed is usually of the first importance. The sight of Lowell's sewers is better proof of the contamination of Lawrence's water supply than any amount of chemical or bacterial analysis. In this case, analysis is useful in measuring the amount of pollution, and in showing any purification which may have taken place. In the case of ground waters, inspection of the water-shed is often impossible, because its exact location is unknown. In these cases, thanks to the great progress which has been made in the methods of examination, we may depend with confidence upon chemical analysis, to show us the past history of a water. The analysis is especially satisfactory where the normal chlorine is accurately known. The normal nitrate is also useful in this connection. In Massachusetts, strictly unpolluted ground waters rarely have as much as 0.02 part nitrogen as nitrate per hundred thousand, and as this does not depend upon proximity to the ocean, it can be used where the normal chlorine is unknown.

If we can show that a water is absolutely free from sewage contamination, we may safely infer the absence of pathogenic germs, although as yet too little is known of the diarrhoea and other complaints which have been sometimes attributed to the use of water quite free from sewage.

The adaptability to public use of a sewage-free water depends mainly upon its physical characteristics—turbidity, color, odor, taste, and hardness. On these points the public is a competent

judge of what is required ; the chemist makes accurate comparison between different waters, but it is for the consumers to say what is satisfactory to them.

If we find that a water-shed is inhabited, or if the chlorine and nitrate are above the normal for the region, then we must conclude that the water is polluted, and other data must be obtained before we can decide upon its quality. The possibility of securing water entirely free from sewage contamination is rapidly becoming less. With increasing population, water-sheds of sufficient size are fast becoming settled, and in those portions of the country where the entire surface of the land is suited to human occupation, and especially in the neighborhood of large cities, their retention for water supply is practically impossible.

We are thus forced to face the problem of so managing an inhabited water-shed, and the water derived from it, as to secure a water supply, which, although it has been polluted, is without danger to the public health.

The question now to be considered is whether pathogenic germs could survive from the point of contamination to the point of consumption. It is not enough to show that they are not now present in the water. It must also be shown that they could not be present under any possible, or at least, probable, conditions. It is our greatest problem to determine through what conditions pathogenic germs can survive.

In its simplest form we have the case of sewers emptying directly into a water course which is used for water supply. There has been a theory current that rivers have a power of purifying themselves, and that when the volume of sewage is not too large in comparison with that of the water into which it flows, the great dilution and the oxidizing action of the air will soon restore the water to its original purity.

Lawrence, Lowell, Albany, and other cities, knowing that their water supplies were polluted, have depended upon these agencies to purify them, and they have depended in vain. Their factors of safety were too small ; the Merrimack and the Hudson were not large enough ; the distances and times were too short ; the germs survived, and increased death rates amounting to epidemics were the results. The experience thus dearly obtained, with the loss

of hundreds of human lives, has taught us lessons far more valuable than any laboratory experiments, however interesting the latter may be. We have learned that extreme dilution, even so great that the most delicate chemical tests do not with certainty show the presence of sewage; that running for a few miles in a large and well aerated river; that storage in a reservoir capable of holding one or two weeks' supply of water, and that the passage through miles of iron pipes under pressure; that each and all of these conditions are inadequate to render a water safe.

Prof. Sedgwick has shown, in his admirable report upon the sanitary condition of Lowell, that after the Merrimack water had passed through the capacious reservoir, and several miles of pipes, requiring in all at least several days, the total number of bacteria was greatly reduced, and apparently also, the number of typhoid germs, for there were relatively less cases among the users of this water than among those who drank the canal water taken more directly from the river.

It is possible that these conditions might be so extended as to secure immunity, or at least, to so decrease the number of disease germs, that their presence would be without noticeable effect upon the public health. In view of our experiences, we shall do well to inquire what limits, if any, are admissible, and in the mean time take good care to avoid all water supplies taken without filtration from bodies of water into which sewage directly flows. Until we have positive information that the objectionable germs cannot live beyond certain limits, we can only be justified in refusing to allow any limits, and in condemning all waters so polluted.

As a solution to our problem, we may have recourse to some method of purification, either of the sewage before turning it into the water, or of the water after it has been polluted. The only processes now known, which are at once feasible and effective in the removal of bacteria, are processes of filtration. Filtration may take place either through natural soil or through specially prepared filters. In either case it may, or it may not, be an efficient safeguard against sewage contamination. Many household filters are notoriously inadequate; many old wells are unmistakable carriers of disease drawn through the soil from neighboring cess-pools, while, on the other hand, people drink with impunity the

water from other wells, even more grossly polluted, but in soils which are more favorable to the removal of bacteria, and in some European cities, a great reduction of the death rate from typhoid fever is effected by the introduction, not of a sewage-free water, but of a well filtered, although previously polluted water.

The sewage of the inhabitants of a drainage area may be filtered, either from cesspools connected with each house, in which case their contents slowly soaks or filters through the soil toward the water course, or the sewage may be collected and treated by intermittent filtration. In either case great care must be taken that no trace of sewage finds a more direct channel than was intended.

Intermittent filtration is only able to exclude bacteria from the effluent under particular conditions, and these conditions must be fulfilled to insure safety. The experiments of the Massachusetts State Board of Health, conducted under the direction of Mr. Hiram F. Mills, have shown what many of those conditions are. I have no time at present to discuss these experiments; I can only refer to the published report, and say that so much light has been obtained as to make possible reliable estimates of the results to be obtained under a wide range of local conditions.

Another way of approaching the problem is to allow the free entry of sewage into the water courses, depending upon filtration to remove the bacteria before it is finally delivered to consumers. In the case of a large inhabited water-shed, as for instance, that of one of our large rivers, this is the only practicable way, it being impossible to maintain adequate inspection of a large area and population.

When extensive sand deposits occur along the banks of the river or lake, wells or filter galleries sunk in them have often yielded a large amount of water, so well filtered by its passage through the sand as to be quite safe. Under other local conditions, similar wells have failed to yield the quantity or quality desired. This method of filtration is most important, but as yet no general conclusions can be safely drawn.

Where there are no sand deposits to make wells and filter galleries successful, other forms of filtration have often been used.

Very prominent are the patented mechanical filters, whose essential characteristics are very high rates of filtration through small

bodies of sand, often with the use of chemicals, and under pressure. Such filters have been most successful in removing suspended matters from turbid river waters, rendering them suitable for paper and other manufacturing, and also in improving the appearance of muddy but unpolluted waters. The success of these filters in their proper sphere is great and unquestioned.

We have as yet, however, no proof that they are capable of removing completely the bacteria from sewage polluted waters. Until we have positive evidence that a system of filtration, under all conditions likely to occur in practice, will exclude pathogenic germs, we shall not be justified in approving its use for the purification of a sewage polluted water.

The cleaning of unpolluted waters is another matter, entirely not to be for an instant confounded with the present problem.

In many European cities another and widely different system of filtration is in use. The water to be filtered is taken into large areas of thoroughly underdrained sand, kept continually covered with water, which slowly finds its way through the sand at the rate of one, two, or even three million gallons per acre daily. The results obtained at Berlin are especially valuable, for the engineer in charge, Herr Piefke, has taken into account the removal of pathogenic germs, both as shown by laboratory experiment and by the death rate from typhoid fever from among the users of the water.

Piefke's results show that under conditions sure to occur without most careful superintendence, bacteria pass the Berlin filters in sufficient numbers to increase the death rate, but by giving most careful attention to details, this can be almost entirely avoided. If the filters do not remove every single germ, the number which escape is too small to perceptibly affect the death rate. These results, and those of other European cities, show us that continuous filtration may, or may not be an efficient safeguard against typhoid fever, according to the rate of filtration, the character of the sand employed, and other details of management.

The point is established that filters can be so constructed and managed as to afford relief. We must now endeavor to find how to attain the desired result with the minimum expense; how coarse material can be used with safety; how rapidly can water

be applied to material of various degrees of fineness ; can the best results be obtained by applying the water continuously, or at intervals, with periods of rest between, during which the filter has a chance to drain, drawing air into its pores. These and similar questions require definite answers. Experiments now in progress at the Lawrence Experiment Station were designed to throw additional light upon these points. We know that fine materials and slow rates of filtration tend to give germ free and consequently safe effluents. Some limits are already known, both from the experience of European cities and from our own experiments ; some filtering materials at certain rates of speed give effluents practically free from bacteria. It is possible that we shall learn by further experiment, that somewhat coarser materials, or that higher rates of filtration may be employed without danger. In the meantime, when it seems necessary to take water supplies from bodies of water into which sewage directly flows, we can best secure the public health by the use of filters which are definitely within the known limits of safety.

ON THE DECOMPOSITION OF MINERALS CONTAINING TITANIUM.

BY JESSE JONES.

In attempting to conduct the analysis of a very refractory mineral containing titanium, magnesium, chromium, etc., according to the method given by Chatard*, it was found very difficult to secure complete decomposition of the mineral by the use of hydrofluoric and sulphuric acids as detailed. Repeated fusions with potassium pyrosulphate while decomposing the mineral introduced large quantities of salts, and was very tedious.

These difficulties led me to seek some method that would give more satisfactory results. The following was finally adopted : 2 gms. of the mineral were placed in a pressure bottle, to which was added 20 cc. of water and 20 cc. of strong sulphuric acid. The ground glass stopper not fitting air tight, a small sheet of pure rubber was interposed. The bottle and contents were placed in an ordinary air bath, and kept at 200 degrees C. for two hours. The residue weighed .018 gms., and was mainly silica. On treatment with hydrofluoric acid but .002 gms. of residue remained.

*This Journal, 5, 163.

A temperature of 200 degrees C. was found to melt the rubber somewhat, but a longer exposure at a lower temperature gave equally good results. As the resulting solution showed a tendency to gelatinize, water was added to it, taking care not to allow it to touch the heated sides of the bottle. The refractory nature of the rock may be judged from the fact that it contained over 7 per cent. MgO , 14 per cent. Al_2O_3 , and considerable amounts of titanium and chromium, which have not yet been determined. By using ammonium salts in the subsequent operations, they can be expelled by nitric acid, and potash and soda if present in the mineral can be determined.

If a pressure bottle is not at hand, one can easily be improvised. The writer found an old bromine bottle sufficiently strong.

ALLEGHENY, PA., 94 Buena Vista St.
Nov. 2, 1891.

THE USE OF CADMIUM IN ASSAYING GOLD BULLION.*

BY CABELL WHITEHEAD, Assayer to the Mint Bureau.

Cadmium, as a substitute for silver in assaying gold bullion, was first used by Balling†. He states that the gold is entirely parted from all metals, except the platinum group, when its alloy with cadmium is boiled with strong nitric acid for one hour, followed by a second boiling for ten minutes with a fresh portion of the same acid. For general assays of gold bullion, I do not think that Balling's method with cadmium will bear comparison in point of accuracy with the old one of quartation with silver and cupellation. But, with certain modifications which will be suggested later, it will be found rapid and satisfactory for a preliminary assay.

It is, however, in the estimation of small quantities of silver in gold bullion containing considerable amounts of copper or platinum, that I have found cadmium to be a most efficient aid.

The difficulty in determining silver in the presence of platinum by cupellation is well known to assayers. In such cases the following has been the method in the United States Mint at Philadelphia:

An approximate assay is made by cupellation, after which,

*Read before the Franklin Institute, Sept. 15, 1891.

†Crooke's Select Methods of Chemical Analysis.

and based on this approximation, enough pure silver is added to 500 mgs. of the bullion to make in all at least 1,004 mgs. of silver present in the assay. This weighed silver and bullion is wrapped in a sheet of lead weighing 2.5 gms., and the whole placed on a hot cupel in the muffle furnace.

As soon as the lead "clears" the cupel is withdrawn, when cold the button is flattened and put in a bottle such as is used in the humid assay of silver, dilute nitric acid is added and heat applied. When action ceases, the silver present in solution is determined volumetrically as usual. The silver found, less the amount added gives the silver in 500 mgs. of bullion.

There are two objections to this method ; (1) The insolubility of lead nitrate in nitric acid necessitates the use of dilute acid, which leaves much alloy with the gold ; (2) the alloy to be removed is one-third silver. This is very important when small quantities of silver are to be determined, as in the case of gold coin, which rarely contains more than .003. Cornets, after three boilings with acid (ten minutes each), retain from .001 to .002 of silver ; so it will be seen at a glance that the amount retained after one boiling with dilute acid will be much greater and the gold residue will contain more silver than was present in the original bullion.

The presence of ten per cent. or more of copper in high grade gold bullion makes the accurate determination of silver by cupellation impossible. Not only is gold taken into the cupel in large quantities by the copper, but it is also left in specks over the entire surface covered by the assay, thus making a "proof" practically worthless.

The method which I am about to describe, was devised for the estimation of silver in gold coin, and has been in use in the laboratory of the Bureau of the Mint for the past year, where it has given such satisfactory results that it is thought a brief description may prove of interest to others engaged in the same line of work.

Five hundred mgs. are weighed into a porcelain crucible and covered with ten gms. of potassium cyanide. The potassium cyanide is melted over a Bunsen burner or preferably a blast lamp. When the cyanide is in quiet fusion one gm. of cadmium is dropped into the crucible, where it quickly melts and forms a bright homogeneous alloy with the gold. After gently shaking,

so as to bring the cadmium in contact with every particle of bullion, the crucible is removed and the contents poured on a clean porcelain slab, where it soon solidifies. The alloy will be found in one piece and easily detached from the potassium cyanide. It is now washed in warm water, dried and placed in a diamond mortar, when several sharp blows with a hammer quickly reduce it to powder.

This powder is carefully transferred to an assay bottle, 1004 mgms. of pure silver added and 10 cc. of nitric acid—32° Baumé—poured on. In from five to ten minutes (depending upon the heat used) the solution is complete and all action has ceased. The bottle is now cooled, 100 cc. of normal salt solution is charged, and the bottle shaken. The precipitation is finished with the decinormal solution.

This assay is accompanied by another called a "proof," made of 1004 mgs. of pure silver dissolved in the same amount of acid. Now the excess of silver found in the assay over that shown in the "proof," is the amount contained in 500 mgs. of coin. This doubled gives parts of silver per thousand.

Example: An alloy composed of 499 mgs. pure gold, one mg. of silver and one mg. of cadmium, treated as above described, after being charged with 100 cc. normal salt solution, required five cc. decinormal solution for complete precipitation of the silver present. A proof assay, carried along as check, upon 1004 mgs. of pure silver, required in addition to 100 cc. of normal salt solution, four cc. of decinormal solution for complete precipitation = to 1004 cc. decinormal solution. Hence, each cc. decinormal equals one mg. silver, and one cc. decinormal solution required by the bullion, in excess of that called for by the silver added, shows the bullion to contain one mg. silver in 500, or two parts per thousand.

It may be asked by those not familiar with mint appliances and usages, "Why not titrate directly the silver brought into solution with the cadmium instead of adding a known weight of pure silver and finding the desired result by difference?"

The reply is that the small amount of silver present in this class of bullion would, as chloride, not "clear" on shaking, and much time would be consumed in finding the end reaction. By the method described the usual apparatus and solutions may be availed of and results rapidly obtained.

When no such reasons exist the sulphocyanide method alluded to at the end of this article is recommended.

EXAMPLE IN GOLD BULLION.

An approximate assay gives by cupellation .035 silver, hence, 500 mgms. will contain about 17.5 mgs. of that metal, and 986.5 mgs. must be added to bring the total silver up to 1004 mgs. If copper is not present, about 50 mgs. is added, it being found that the alloy of copper with cadmium is very brittle, and the resulting button is easily crushed to powder.

The sample having been fused with cadmium in presence of potassium cyanide is powdered and subjected to treatment with nitric acid as above described.

After charging with 100 cc. normal salt solution, and shaking, the assay required 4.5 cc. decinormal solution for end reaction. A "proof" consisting of 1004 mgs. pure silver in solution, treated in same manner, required but 3 cc. decinormal solution.

Hence the assay contained $4.5 - 3 = 1.5$ mgs. more silver than the proof, or $1004 + 1.5 = 1005.5$ mgs. in silver in all. This, less the 986.5 mgs. silver purposely added gives 19 mgs. as the silver present in 500 mgs. of bullion taken, or thirty-eight parts in each thousand instead of thirty-five parts found by cupellation.

In favor of the new method it may be said :

(1) That the ready solubility of cadmium in nitric acid of any strength, makes it possible to dilute (if the term may be used), the silver present in gold bullion, to any desired extent, while on the other hand the difficult solubility of lead necessarily limits the dilution possible by the time required for its even imperfect extraction.

The inevitable small portion of other metals retained by the gold after treatment with nitric acid may therefore, by the use of cadmium, be made to contain but an infinitesimal quantity of silver.

(2) The brittleness of the button obtained, permits its being crushed to a powder, in which condition the alloy rapidly yields its soluble portion to nitric acid, and the time required for an assay is materially shortened.

(3) The low temperature required enables the chemist to dispense with all special appliances. A Bunsen burner will well

answer the requirements for heating purposes, and little more is needed beyond a standard salt solution. No muffle or rolls are wanted.

In a laboratory where few assays are made the following method might be followed and very satisfactory results obtained. After alloying and crushing, treat in a parting flask with 15 cc. of nitric acid 32° Baumé for ten minutes, pour off this acid into a beaker, add fifteen cc. acid same strength and boil for ten minutes longer, pour off again in same beaker, wash with hot water and take out in an annealing cup, dry and heat over blast lamp, weigh and deduct .25 mgs. for cadmium retained. Twice this weight gives the gold fineness.

The acid and washings are evaporated to drive off free nitric acid, and silver determined either as chloride, or volumetrically with sulphocyanide with ferric indicator. Cadmium nitrate does not interfere in the least with the determination of silver, either as chloride or as sulphocyanide.

THE DIRECT DETERMINATION OF ALUMINUM IN IRON AND STEEL,*

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The unsatisfactory character of most, if not all, of the processes for the direct determination of alumina in the presence of iron and phosphoric acid, and the sharpness with which both the iron and phosphoric acid can be determined, have led chemists to rely mainly on processes in which the alumina is obtained by difference. But in the modern alloys of aluminum and iron, where the aluminum may be present only to the extent of a small fraction of one per cent., nothing short of the isolation of the alumina itself can give satisfactory evidence of its presence.

In the course of some experiments on the electrolytic deposition of metals, we have found that it is possible to remove iron completely from its acid solution in large quantity and in short time, by a current that will not in the least affect the alumina in solution. The essential condition of success in this operation is the use of mercury as a cathode, the iron forming an amalgam with the mercury as fast as it is deposited from solution. This use of mercury was

*Read at the Cleveland Meeting American Inst. of Mining Engineers.

proposed by Dr. Wolcott Gibbs, in a paper read before the National Academy of Science in 1883, as a method of determining many metals by electrolysis which are not at all, or only imperfectly, deposited on a platinum cathode. It is certainly one of the most valuable and suggestive contributions to the quantitative separation and determination of metals by electrolysis that has yet been made.

The following are some of the experiments we have made to determine the conditions of success in the application of the method to the determination of aluminum in the presence of iron.

First, as to the completeness of the precipitation of the iron. The first attempt to determine the iron which had been removed from the solution and alloyed with the mercury showed an apparent loss, notwithstanding the fact that the iron was completely removed from solution. This was subsequently found to be due to the volatilization of some of the mercury on drying before weighing. The amount of mercury which may be thus lost is very considerable, as the following experiments show.

About 75 gms. of mercury were put into a beaker, which was then weighed. It was washed several times with water and once or twice with alcohol. The loss on drying different times and at different temperatures was as follows :

Time of Drying.	Temperature.	Loss, Gram.
10 minutes.	140° C.	.0096
"	100°	.0043
"	"	.0028
"	"	.0030
"	"	.0030
"	"	.0025
2 hours.	70°	.0040
5 "	"	.0120
20 "	"	.0520
48 "	25°	.0030
48 "	24°	.0025
24 "	"	.0007
24 "	"	.0012
48 "	"	.0042
48 "	"	.0033

But it is, in fact, only necessary to heat the mercury for about two minutes at a temperature of 100° C. to free it completely from moisture, and in this time the loss is very small. The following are

the amounts lost in nine experiments under these conditions : .0002, .0005, .0005, .0003, .0008, .0005, .0002, 0, 0, an average of 0.00033 gram.

There seems also, at times, to be a loss not connected with the volatilization of the mercury, which, possibly, may be due to impurities in the mercury, metals, for instance, which are dissolved out by the acid, and not precipitated on the mercury again. On this account it is desirable, in cases where the process is used to determine iron or other metal, to have a blank beaker in the circuit, containing only the mercury and dilute sulphuric acid, and to add any loss which may be found in this beaker to the amount found in the others in the series.

The following are a series of results obtained by electrolyzing a solution of ferrous ammonium sulphate, slightly acidulated with sulphuric acid.

Iron Taken. Gram.	Iron Found. Gram.	Loss of Weight in Blank. Gram.	Iron Found + Loss in Blank. Gram.
.2260	.2254	Not made.	
.3727	.3725	"	
.3080	.3089	"	
.3238	.3232	"	
.0647	.0632	.0020	.0652
.0647	.0634	Not made.	
.0647	.0649	0000	.0649
.0647	.0635	Not made.	
.0604	.0602	.0003	.0605
.0604	.0608	.0003	.0611
.3020	.3008	.0003	.3011
.3020	.3000	.0003	.3003

The best conditions for the rapid precipitation of the iron are a strong current (about 2 amperes, or 20 cc. of electrolytic gas a minute), a nearly neutral solution of small bulk, a large amount of mercury (not less than fifty times the weight of the iron to be precipitated), and a large anode of platinum. The mercury cathode is brought into the circuit by means of a platinum wire inclosed and fused into one end of a glass tube, which passes through the liquid. It is of advantage to pour mercury into this tube to the depth of an inch, in order to weight it and make the connection with the mercury cathode more stable.

By observing the above conditions it was found practicable to

precipitate 10 gms. of iron in from 10 to 15 hours. The iron amalgam may contain as high as 10 per cent. of iron. On standing a long time exposed to the air, the iron separates out as a black powder, which may be removed from the mercury by agitation with water. Mercury which has been used for iron precipitations may be purified by removing the greater part of the iron amalgam by filtration through chamois skin, and then passing air through the filtered portion, as recommended by J. M. Crafts.

Second, as to the behavior of manganese in solution under the foregoing conditions. Inasmuch as manganese is almost always present in iron and steel, a good many experiments were made to find what becomes of it under the electrolytic conditions which we have been considering. It was found that a portion is oxidized to the dioxide, coating the platinum anode, and ultimately falling off, in great part, in scales, and that a portion is reduced to the metallic state and alloys with the mercury. This fact of the reduction of the manganese was evident on electrolyzing a solution containing only dilute sulphuric acid, using as a cathode mercury which had been previously used in an experiment with a manganese solution. In a few minutes the permanganate color appeared, and a slight coating of manganese dioxide was deposited on the anode. The experiments made to determine what proportion of manganese was reduced and what proportion oxidized were not satisfactory, but in general it may be said that about half the manganese alloys with the mercury; the other half is nearly all oxidized, and is found on the anode and in scales floating in the liquid. A small portion is always found in solution. By using both electrodes of platinum it was found possible, in the absence of iron, to precipitate manganese completely as dioxide; but the coating on the anode was never coherent when more than mere traces of manganese were present. But the danger of the re-solution of the floating particles of the manganese dioxide, together with the necessity of filtering and igniting it to the proto-sesquioxide, makes the process an unsatisfactory one for the determination of manganese. The best conditions were found to be a concentrated solution of manganese sulphate to which a little nitric acid had been added, a rather weak current, a small cathode and a large anode.

Third, as to the influence of phosphoric acid on the precipitation

of iron. Two solutions containing equal amounts of iron were electrolyzed in series. To one was added one gm. of crystallized hydrogen di-sodium phosphate, and to the other dilute sulphuric acid. When the iron was all precipitated, the beakers with the mercury, together with the glass tubes containing the platinum wires, were weighed, and found to have gained, respectively, 0.1290 and 0.1275 gm. To a solution of 3 gms. of iron in sulphuric acid, 0.1935 gm. crystallized hydrogen di-sodium phosphate was added, equivalent to .0167 phosphorus. After the iron was completely removed from the solution, the phosphoric acid was precipitated by magnesium mixture and .0163 gm. phosphorus obtained. A duplicate experiment gave .0161 gm. phosphorus. A third experiment with the same amount of iron gave, under like conditions, .0064 gm. phosphorus when .0068 was added. From the experiments we may conclude that the separation, by this electrolytic method, of iron and phosphoric acid in solution is satisfactory.

Fourth, as to the separation of iron and aluminum. Known amounts of iron and aluminum in solution together as sulphates were electrolyzed, and, after all the iron had been deposited, the alumina, was precipitated by ammonia. Following are two results thus obtained.

Alumina Taken. Gram.	Alumina Found. Gram.	Iron Taken. Gram.	Iron Found. Gram.
.0283	.0286	.2286	.2277
.0142	.0142	.2286	.2283

The iron, determined by weighing the mercury after electrolyzing the solution, includes in both cases a blank of .0020 gm., which was the loss of a mercury cathode in the same series, when sulphuric acid only was electrolyzed.

The process was now tried under the conditions which would obtain in the determination of aluminum in iron and steel, namely, known amounts of aluminum sulphate were added to a known amount of steel. After much experimenting the following procedure was adopted as being the most uniformly satisfactory.

Dissolve 5 to 10 gms. of iron or steel in sulphuric acid, evaporate until white fumes of sulphuric anhydride begin to come off, add water, heat until all the iron is in solution, filter off the silica and carbon, and wash with water acidulated with sulphuric acid. Make the filtrate nearly neutral with ammonia, and add

to the beaker in which the electrolysis is to be made, about one hundred times as much mercury as the weight of iron or steel taken. The bulk of the solution should be from 300 to 500 cc. Connect with the battery or dynamo current in such a way that about two amperes may pass through the solution over night. This we have generally accomplished by using three lamps 32-candle power arranged in parallel on an Edison circuit. In the morning the solution is tested for iron, and, if necessary, the electrolysis is continued after adding enough ammonia to neutralize the acid that has been set free by the deposition of the iron. The progress of the operation may be observed by the changing color of the solution. At first it becomes darker in color near the anode; after five or six hours it is nearly colorless, and finally becomes pink, from the formation of permanganate.

When the solution gives no test for iron, it is removed from the beaker with a pipette while the current is still passing. When as much has been removed as possible without breaking the current, water is added and the operation continued until the acid has been so far diluted that there is no danger of dissolving iron from the mercury. The anode is now taken out and the mercury washed with water until the last traces of the solution have been removed from it. After filtering, to remove any flakes of manganese dioxide which may be suspended in the solution, sodium phosphate is added in excess and 10 gms. of sodium acetate. The solution is now made nearly neutral with ammonia and boiled for not less than forty minutes. The precipitate of aluminum phosphate is then filtered off, ignited and weighed. It should be white after ignition. If it has more than the faintest shade of color it must be dissolved by fusing with acid potassium sulphate and again electrolyzed for two or three hours. The second precipitate has been found to be always white without a trace of iron, but, in general, we have found the first precipitate to be free from iron or to contain such a minute amount that the second treatment is not necessary. We have determined that .0003 gm. of iron will give a decided red color to .0076 gm. of aluminum phosphate. The precipitate of aluminum phosphate, produced as above, does not always have the composition $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. Our analyses of it go to show that the formula $7\text{Al}_2\text{O}_3 \cdot 6\text{P}_2\text{O}_5$ more nearly expresses its aver-

age composition, and in those cases in which the amount of phosphoric acid and alumina have not been actually determined in the precipitate, we have assumed this composition, which is equivalent to 24.14 per cent. of aluminum in the precipitate.

It is necessary to boil for at least forty minutes to precipitate completely the aluminum phosphate, and excessive washing of the precipitate should be avoided.

The following table gives the results obtained in determining by the above process the aluminum added in known amounts to solutions of steel.

Steel Taken. Grams.	Per Cent. of Aluminum Added.	Per Cent. of Aluminum Found.
5	0.39	0.36
5	0.39	0.38
5	0.39	0.38
5	0.39	0.38
5	0.39	0.37
5	0.043	0.045
5	0.043	0.041
5	0.043	0.049
5	0.043	0.048
10	0.027	0.015
10	0.200	0.160
10	0.046	0.044
5	0.085	0.088

A blank experiment with the same steel, without the addition of any aluminum, gave a precipitate of aluminum phosphate equivalent to 0.004 per cent. of aluminum, which has been deducted from the results in the above determinations. This small amount came, doubtless, from the reagents and the glass vessels used, and may have been partly silica. This correction should be made in all cases where the amount of aluminum is very small.

A sample of Mitis steel analyzed by this method gave the following result :

Steel Taken. Gram.	Aluminum Found. Per Cent.
4.4260	0.014
4.4260	0.013
12.6650	0.014

A sample of "aluminum physic" used in the preparation of Mitis castings gave as follows :

PURIFICATION OF WATER BY FREEZING.

Iron Taken. Grams.	Aluminum Found. Per Cent.
1.6130	6.28
0.4030	6.52
0.4030	6.22

A sample of pig-iron to which aluminum had been added in remelting gave as follows :

Iron Taken. Grams.	Aluminum. Per Cent.
1.4576	0.789
1.8167	0.806
1.6390	0.794
1.6130	0.802

It might be thought that the process would be simplified by reducing the iron to the state of protoxide, and then precipitating alumina as basic acetate, subsequently removing by electrolysis the small amount of iron precipitated with the alumina. A number of experiments proved, however, that this modification not only gave less accurate results, but involved much more work than the precipitation of all the iron by electrolysis. When the iron is all removed over night without involving any work on the part of the analyst, it is surely superfluous to go through a more or less tedious chemical operation to remove a part of the iron.

It is obvious that this process of electrolysis with a mercury cathode may be of value in other analytical operations in which the removal of the iron would be of advantage : as, for instance, in the determination of phosphoric acid by magnesia.

PURIFICATION OF WATER BY FREEZING.

BY WM. P. MASON.

The old notion that water completely purifies itself by freezing has by no means died out, and even after Pruden's able report on the contaminated condition of much of the public ice supply, we find educated people collecting ice from sources so polluted as to be beyond question unfit to furnish drinking water. A somewhat aggravated case of this kind having presented itself, the following experiments were undertaken to outline the relation existing between an ice and the water from which it is frozen. The materials employed for experiment were mixed with ordinary tap water. The given weights are in grams per 100 cc. of water.

	Total Residue from 100 cc.	Loss on Ignition. Volatile and Organic Matter.	Inorganic Residue.	Per cent. of the Mineral Matter Originally in the Water yet Remain- ing in the Ice.	Per cent. of Organic and Volatile Matter of the Water yet remain- ing in the Ice.
100 cc. urine diluted to 10 liters0285	.0070	.0215		
Ice from same0023	.0022	.0001	0.46	31.43
500 cc. urine diluted to 10 liters1380	.0469	.0911		
Ice from same0389	.0213	.0176	19.32	45.41
10 cc. urine in 10 liters of water0112	.0047	.0065		
Ice from same0040	.0018	.0022	33.84	38.21
100 cc. glycerine diluted to 10 liters7951	.7911	.0040		
Ice from same1012	.1005	.0007	17.50	12.70
50 gms. sugar dissolved in 10 liters water4932	.4860	.0072		
Ice from same1373	.1360	.0013	18.05	27.98
50 gms. NaCl in 10 liters water5013	0	.5013		
Ice from same1449	0	.1449	28.9	
10 liters of water tinted with indigo0399	.0336	.0063		
Ice from same0027	.0027			8.03
10 liters H ₂ O, with a little egg albumen, i.e., 1/2 of that in one egg0163	.0119	.0044		
Ice from same0038	.0031	.0007	15.91	26.05
10 gms. Na ₂ CO ₃ in 10 liters of water0907	.0038	.0869		
Ice from same0180	.0025	.0155	17.83	65.78
10 gms. sugar in 10 liters of water1045	.0996	.0049		
Ice from same0118	.0100	.0018	36.73	10.04
10 gms. oxalic acid in 10 liters of water0129	.0067	.0062		
Ice from same0037	.0022	.0015	24.19	32.82
10 gms. glycerine in 10 liters of water0187	.0140	.0047		
Ice from same0028	.0010	.0018	38.30	7.14
Troy City supply0092	.0035	.0057		
Ice from same0010	.0010	trace	0	28.5
Very hard spring water0540	0	.0540		
Ice from same0045	0	.0045	8.3	
Water from Erie Canal where public ice supply is taken0112	.0033	.0079		
Ice from above locality used for public supply0067	.0025	.0042	53.2	75.7

Dilute sulphuric acid was prepared of a strength = .3280 gms. H₂SO₄ per liter. The ice from same when melted retained H₂SO₄ corresponding to .0390 gms. per liter. Ice retained 11.89 per cent. of the H₂SO₄ in the water.

From the foregoing it will be observed that organic impurity is more liable than mineral matter to pass into ice, and, inasmuch as the organic impurity is the more objectionable of the two, the distinction is important. It will be noticed that the waters contain-

ing sewage and urine formed ices of the greatest organic percentages.

Of the fifteen waters containing organic impurity, the percentages of such impurity retained by the ice varied from 7.14 per cent. to 75.75 per cent., with an average of 34.3 per cent, while of the eighteen waters holding mineral impurity, the ices formed therefrom retained from a trace to 53.20 per cent. of such impurity, with an average of 21.2 per cent.

RENSSELAER POLYTECHNIC INSTITUTE,
Nov. 16, 1891.

NINTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its ninth annual report.

Since our last meeting the following bibliographies have been printed :

1. A Bibliography of Geometrical Isomerism. Accompanying an Address on this subject to the Chemical Section of the American Association for the Advancement of Science at Indianapolis, August, 1890, by Prof. Robert B. Warder, Vice President. Proceedings A. A. S., Vol. XXXIX. Salem, 1890. 8 vo.

2. A Bibliography of the Chemical Influence of Light ; by Alfred Tuckerman. Smithsonian Miscellaneous Collections No. 785, Washington, D. C., 1891. pp. 22. 8 vo.

3. A Bibliography of Analytical Chemistry for the year 1890, by H. Carrington Bolton. J. Anal. Appl. Chem. v, No. 3. March, 1891.

We chronicle the publication of the following important bibliography.

A Guide to the Literature of Sugar. A book of reference for chemists, botanists, librarians, manufacturers and planters, with comprehensive subject-index. By H. Ling Roth, London, Kegan Paul, Trench, Trübner & Co. 1890. 8 vo. pp. xvi-159,

This work contains more than 1,200 titles of books, pamphlets and papers relating to sugar. Many of the titles are supplemented with brief abstracts. The alphabetical author-catalogue is followed by a chronological table, and an analytical subject-index. The compilation extends to the beginning of the year 1885, and

*From Advance proof-sheets of the Proceedings of the American Association for the Advancement of Science, Washington meeting, 1891.

the author promises a supplement and possibly an annual guide.

This ambitious work is useful but very incomplete; it does not include glucose. The author gives a list of fifteen periodicals devoted to sugar, and omits exactly fifteen more recorded in Bolton's *Catalogue of Scientific and Technical periodicals* (1665-1882). (Washington, 1885). Angelo Sala's *Saccharologia* (Rostock, 1637) is not named, though mentioned in Roscoe and Schorlemmer and elsewhere. Notwithstanding some blemishes this work is indispensable to chemists desirous of becoming familiar with the literature of sugar. It is to be hoped that a second edition brought down to date may be issued by the author.

4. A Bibliography of Ptomaines accompanies Prof. Victor C. Vaughan's work. *Ptomaines and Leucomaines*, Philadelphia, 1888. (Pages 296-314). 8 vo.

Chemists will hail with pleasure the announcement that a new Dictionary of Solubilities is in progress by a competent hand. Prof. Arthur M. Comey of Tufts College, College Hill, Mass., writes that the work he has undertaken will be as complete as possible. "The very old matter which forms so large a part of Storer's Dictionary will be referred to, and in important cases fully given. Abbreviations will be freely used and formulæ will be given instead of the chemical names of substances, in the body of the book. This is found to be absolutely necessary in order to bring the work into a convenient size for use. . . . The arrangement will be strictly alphabetical. References to original papers will be given in all cases . . ."

Professor Comey estimates his work will contain over 70,000 entries and will make a volume of 1,500 to 1,700 pages.

The following letter from Mr. Howard L. Prince, Librarian of the U. S. Patent Office, explains itself.

UNITED STATES PATENT OFFICE.

Washington, D. C., February 11, 1891.

DR. H. CARRINGTON BOLTON, University Club, New York, N. Y.

DEAR SIR :—In response to your request I take pleasure in giving you the following information regarding the past accomplishments and plans for the future of the Scientific Library in the matter of technological indexing.

The work of indexing periodicals has been carried on in the Library for some years in a somewhat desultory fashion, taking up one journal after

another, the object being, apparently, more to supply clerks with work than the pursuance of any well-defined plan. However, one important work has been substantially completed, viz. : a general index to the whole set of the Scientific American and Supplement from 1846 to date.

It is unnecessary for me to point out to you the importance of this work embracing a collection which has held the leading place in the line of general information on invention and progress, the labor of compiling which has been so formidable that no movement in that direction has been attempted by the publishers except in regard to the supplement only, and that very imperfectly. This index embraces now one hundred and eighty-four thousand cards, not punched, and at present stored in shallow drawers and fastened by rubber bands, and of course, they are at present unavailable for use. There is little prospect of printing this index and I have been endeavoring for some time to throw the index open to the public by punching the cards and fastening them with guard rods, but as yet have made no perceptible impression upon the authorities although the expense of preparation would be only about \$70.00.

There has also been completed an index to the English journal "Engineering," comprising eighty-four thousand cards, from the beginning to date.

An index to Dingler's Polytechnisches Journal was also commenced as long ago as 1878, carried on for six or seven years and then dropped. I hope, however, at no remote date, to bring this forward to the present time.

On taking charge of the library I was at once impressed with the immense value of the periodical literature on our shelves and the great importance of making it more readily accessible, and have had in contemplation for some time the beginning of a card index to all our periodicals on the same general plan as that of Reith's Repertorium. I have, however, been unable to obtain sufficient force to cover the whole ground, but have selected about one hundred and fifty journals, notably those upon the subject of chemistry, electricity and engineering, both in English and foreign languages, the indexing of which has been in progress since the first of January. This number includes substantially all the valuable material in our possession in the English language, not only journals, but transactions of societies, all the electrical journals and nearly all the chemical in foreign languages. This index will be kept open to the public as soon as sufficient material has accumulated. In general plan it will be alphabetical, following very nearly the arrangement of the periodical portion of the Surgeon-General's catalogue. I shall depart from the strictly alphabetical plan sufficiently to group under such important subjects as chemistry, electricity, engineering, railroads, etc., all the subdivisions of the art, so that the electrical investigator, for instance, will not be obliged to travel from one end of the alphabet to the other to find the divisions of generators, conductors, dynamos, telephones, telegraphs, etc., and in the grouping of the classes of applied science the office classification of inventions will, as a rule, be adhered to, the subdivisions being, of course, arranged in alphabetical order

under their general head and the title of the several articles also arranged alphabetically by authors or principal words.

With many thanks for the kind interest and valuable information afforded me, I remain,

Very truly yours,

HOWARD L. PRINCE,
Librarian Scientific Library.

The committee much prefers to record completed work than to mention projects, as the latter sometimes fail. It is satisfactory, however, to announce that the indefatigable indexer, Dr. Alfred Tuckerman, is engaged on an extensive Bibliography of Mineral Waters. The Chairman of the Committee expects to complete the MS. of a Select Bibliography of Chemistry during the year, visiting the chief libraries of Europe for the purpose this summer.

H. CARRINGTON BOLTON, *Chairman*,
F. W. CLARKE,
ALBERT R. LEEDS,
ALEXIS A. JULIEN,
JOHN W. LANGLEY,
ALBERT B. PRESCOTT.

[Dr. Alfred Tuckerman was added to the committee at the Washington meeting to fill a vacancy].

A METHOD FOR THE SEPARATION OF ANTIMONY FROM ARSENIC BY THE SIMULTANEOUS ACTION OF HYDROCHLORIC AND HYDRIODIC ACIDS.*

BY F. A. GOOCH AND E. W. DANNER.

A method for the separation of arsenic from antimony based upon the difference in volatility of the lower chlorides was introduced originally by Fischer.† This method of treatment consisted in the reduction of the chlorides by means of ferrous chloride and the volatilization of the arsenic by repeated distillations of the mixture with hydrochloric acid of twenty per cent. strength added in successive portions. The process has been subsequently modified by Hufschmidt‡ by the substitution of gaseous hydrochloric acid introduced in continuous current into the distilling mixture,

*Am. J. Sci., Oct., 1891.

†Ann. Chem. u. Pharm. 208, 182.

‡Ber. d. deutsch chem. Ges., xvii, 2245.

for the aqueous acid, and later changed further and improved by Classen and Ludwig,* who employ ferrous sulphate, or ammonio-ferrous sulphate, in place of the less easily prepared ferrous chloride. In its latest form the method is exceedingly exact, but the conditions are such that the antimony in the residue must be determined gravimetrically. It has been our endeavor to so arrange the process that the determination of the antimony may be made by a rapid volumetric method and this we have attempted to accomplish by substituting for the iron salt, which utterly precludes the direct volumetric estimation of the antimony, another reducer—hydriodic acid—which can interfere in no way with the subsequent determination of the antimony by the well known iodometric method.

It has been shown in previous work in this laboratory that arsenic† and antimony‡ may both be reduced by the action of hydriodic acid applied under appropriate conditions. In those processes, however, it was essential that the arsenic should not volatilize, and the conditions were adjusted accordingly. In the present case we have to test the reducing action of hydriodic acid in the presence of strong hydrochloric acid and at the boiling temperature of the solution—conditions arranged to bring about the volatilization of the arsenic as rapidly as possible. Certain preliminary experiments gave indication that a half gm. of arsenic oxide could be completely volatilized by the action of potassium iodide in excess in the manner described, and that an equivalent weight of antimonious oxide (added in the form of tartar emetic) was retained entirely in the residue under similar conditions of treatment. Moreover, it appeared that this action could be brought about in solutions measuring no more than 100 cc. at the beginning and no less than 50 cc. at the end of the distillation, so that a very considerable saving of time over that demanded by the process of distillation as left by Classen and Ludwig could be effected. Accordingly we proceeded to test the action of the hydriodic acid quantitatively, following the same general lines. The distillation apparatus consisted of a flask of 250 cc. capacity, provided with a hollow glass stopper tightly fitted in a ground joint, the stopper

*Ber. d. deutsch. chem. Ges. xviii, 1110.

†Gooch and Browning, Am. J. Sci. vol. x1, p. 66.

‡Gooch and Gruener, Am. J. Sci. vol. xlii, p. 213.

itself being sealed upon a large glass tube bent suitably to connect the interior of the flask with an upright condenser, while through the hollow stopper, and sealed into it, passed a smaller glass tube reaching nearly to the bottom of the flask. The arrangement was such that a current of gas entering the smaller tube would pass nearly to the bottom of the flask and then out through the hollow stopper into the condenser without meeting joints of rubber or cork. Into this flask was weighed, for the experiments of Table I, about a half gram of carefully recrystallized tartar emetic, and a half gram of pure di-hydrogen potassium arseniate and a gram of potassium iodide were added in concentrated solution, the volume of liquid being made up to 100 cc. by the addition of strong hydrochloric acid. A brisk current of hydrochloric acid was passed into the solution through the tube sealed into the glass stopper of the flask until complete saturation was effected, and then the liquid was heated and distilled in the continuous current of hydrochloric acid gas until the volume of 30 cc. was reached. Iodine was evolved as soon as the liquid became warm and the greater part of it passed into the distillate with the first 10 cc. When the final concentration was reached the solution was in each case colorless, but on cooling there appeared in one of the two experiments of this set a pale yellow tint which vanished with the dilution involved in the transfer and washing from the flask previous to titration. The addition of starch to the cooled and diluted liquid developed no color. To the liquid were added 1 gm. of tartaric acid, to keep the antimony in solution during subsequent treatment, sodium hydrate nearly to neutrality, and hydrogen sodium carbonate in excess amounting to about 20 cc. of the saturated solution; and the antimonious oxide in solution was titrated by decinormal iodine standardized against tartar emetic. The details of these experiments are given in Table I.

In Table II are comprised the accounts of experiments similar in general to those of Table I, excepting that the final volume after concentration was a little more, and the antimony was in every case oxidized in alkaline solution by standard iodine previous to the introduction of hydrochloric acid and distillation.

Table III includes the records of experiments similar in every respect to those of Table II, excepting that as starch showed a

slight color in the cooling liquid after distillation, the solution was treated with an excess of sulphurous acid, which was subsequently oxidized exactly by standard iodine previous to neutralization and the final titration.

I.

H ₂ KAsO ₄ taken.	KI taken.	Volume.		Color.		Sb ₂ O ₃ taken.	Sb ₂ O ₃ found.	Error.
		Initial.	Final.	On Cooling.	With Starch.			
gm.	gm.	cc.	cc.			gm.	gm.	gm.
0.5	1.0	100	30	pale yellow	none	0.2282	0.2271	0.0011—
0.5	1.0	100	30	none	none	0.2283	0.2266	0.0017—

II.

0.5	0.5	120	50	none	none	0.2258	0.2235	0.0023—
0.5	0.5	100	50	pale yellow	none	0.2252	0.2235	0.0017—
0.5	0.5	100	50	pale yellow	none	0.2178	0.2163	0.0015—
0.5	0.5	100	50	trace	none	0.2231	0.2231	0.0000
0.5	0.5	100	40	trace	none	0.2261	0.2235	0.0026—

III.

0.5	0.5	100	50	pale yellow	faint	0.2268	0.2265	0.0003—
0.5	0.5	100	50	pale yellow	faint	0.2306	0.2300	0.0006—
0.5	0.5	100	50	pale yellow	faint	0.2272	0.2264	0.0008—

The same general phenomena were observed in all these experiments, and deficiencies in the amounts of antimony indicated, whether the element was present in the lower or higher degree of oxidation before the distillation, appear in all, but most notably in the results of Tables I and II. These losses cannot be attributed, entirely at least, to mechanical transfer in the process, inasmuch as the greater losses are not associated with the greater concentrations; and, furthermore, according to our qualitative experiments made under the conditions of these determinations, no antimony, so far as we could observe, passed into the distillate. If the coloration of liquid on cooling were due to the liberation of iodine by action of air upon the hydriodic acid the iodine thus set free might be counted upon to oxidize a corresponding portion of the antimony in the neutralization, and so to occasion deficiency in the indications of titration. Against this supposition, however,

we have the evidence of experiment that the greatest losses are not found in those cases in which color was developed in the cooling liquid. Moreover, in all cases, excepting those of Table III, starch gave no test for free iodine in the diluted liquid, though it must not be overlooked that the presence of a considerable amount of hydrochloric acid tends to impair the delicacy of the test. If, on the other hand, the color is not due altogether to free iodine it is difficult to account for its development unless it is caused by the formation of antimonious iodide as the solution of strong hydrochloric containing also hydriodic acids cools. On the whole, we are inclined to attribute at least a part of the apparent deficiency to the presence, as the time of neutralization, of a small amount of iodine chloride, which, in accordance with what is known of its modes of formation, might be formed by the oxidizing effect of the antimonious and arsenic oxides upon the mixed acid. At all events, it is evident that if iodine chloride were present we should expect to note the phenomena which we do see; it would give, in small quantity, little or no color to the liquid, would not show the starch reaction for free iodine in the acid solution, and would be destroyed with the formation of hydrochloric and hydriodic acids by the addition of sulphurous acid to the still acid liquid, leaving the antimony unchanged and determinable iodometrically in alkaline solution after the exact oxidation of the excess of sulphurous acid by iodine in acid solution: on the other hand, it would act in alkaline solution like the free halogens and tend to diminish the antimony indicated by titration. Whatever the real cause or causes of the deficiency may be, it appears in the results of Table III that the treatment with sulphurous acid affects the indications favorably. The mean error of three closely agreeing determinations is 0.0006 gm.—and this plainly within the limits of allowable variation in iodometric work with decinormal solutions.

It appears, therefore, that hydriodic acid may be made to serve satisfactorily as a substitute for the ferrous chloride of Fischer's original method, or for the ferrous sulphate of the modification of Classen and Ludwig, the determination of the residual antimony being perfectly practicable. The method of proceeding which we advocate is briefly summarized in the following statement: To the

solution of the oxides of arsenic and antimony, taken in amounts not exceeding 0.5 gm. of each, potassium iodide is to be added in a little more than the equivalent quantity, and enough strong hydrochloric acid to raise the entire volume of the solution to 100 cc. Hydrochloric acid gas is passed into the liquid to saturation as well as during the distillation to follow, and the distillation is carried on until the volume of the liquid decreases to 50 cc. or a little less. The liquid is cooled rapidly, treated first with an excess of sulphurous acid and then with iodine to the exact oxidation of the former reagent; and, after the addition of 1 gm. of tartaric acid to every 0.2 gm. antimonious oxide, the acid present is nearly neutralized with sodium hydrate, the neutralization being completed by hydrogen^o sodium carbonate added in excess to an amount corresponding to 10 cc. of the saturated solution for every 0.1 gm. of antimonious oxide present. Titration with decinormal iodine standardized against tartar emetic gives the antimony quickly and with a fair degree of accuracy. The whole process requires about an hour and a half for completion.

THE PROPERTIES OF PRECIPITATES.

BY E. WALLER, PH.D.

[Continued from page 574.]

PbSO₄

Rem.—Usual precipitant, H_2SO_4 . By digestion with alkaline carbonates or bicarbonates, it is converted to $PbCO_3$.

Cond.—Solution should be acid with H_2SO_4 and contain little or no free HNO_3 or HCl . The larger the proportion of these acids and the warmer the solution, the more H_2SO_4 required. NH_4 salts and salts of organic acids should not be present. Also, any large proportion of chlorides.

Sol.—Readily soluble in concentrated mineral acids, H_2SO_4 , as well as the others, but less soluble in dilute H_2SO_4 than in pure water. Soluble in $Na_2S_2O_3$, in caustic alkaline solutions, and in ammonia salts, notably those of organic acids especially when free ammonia is present. $NH_4C_2H_3O_2$ and $(NH_4)_2C_2H_3O_2$ may be used for this purpose. To obtain $PbSO_4$ for ignition and weighing, the usual procedure is to wash off all other substances with very

dilute H_2SO_4 and then to remove the latter before drying by washing with alcohol.

Contam.—If all other sulphates (than $PbSO_4$) have not been removed by washing with dilute H_2SO_4 , as just described, the precipitate may be contaminated with sulphates, most of which are insoluble in alcohol.

Ign.—Unchanged by a moderate heat. At temperatures usually higher than are ordinarily obtained with a Bunsen burner, the compound may fuse, but without volatilization.

With C partially or entirely reduced to Pb, PbS , etc., which are volatile. The precipitate should be separated from the filter paper, which should be separately incinerated (in the cover of the *porcelain* crucible) with the aid of a few drops of concentrated HNO_3 and H_2SO_4 , the ashes and precipitate united and the whole ignited before weighing.



Rem.—Usual precipitant, $K_2Cr_2O_7$ in solution acid with acetic.

Cond.—Bi, Ba, Ag and Fe should not be present. Solution should not contain chlorides or large amounts of alkaline salts, and should be acid with no stronger acid than acetic. Alkaline citrates, tartrates, etc., should be absent.

Sol.—Dissolved by moderately strong mineral acids and by caustic alkalis. HCl reduces the chromium partially or entirely to Cr_2Cl_6 , more readily in the presence of acetic acid, alcohol or other carbon compounds. Soluble in hot moderately concentrated solutions of $(NH_4)C_2H_3O_2$. Insoluble in very dilute HNO_3 .

Contam.—Possibly Ba, Bi or Hg, chromates, etc. If much Fe is present, the precipitate is likely to contain that element, probably as $Fe_2(CrO_4)_3$.

Ign.—Alone fuses and parts with some oxygen. With C it is more easily decomposed, some metal being reduced. On account of these properties the precipitate is usually dried on a weighed filter for estimation. The Gooch filter in which, if paper is used, it need be only about the size of a five cent piece, is especially advantageous for this purpose.



Rem.—Usual precipitant H_2S . Partially decomposed by drying at $100^\circ C$. Used for separation.

Cond.—Solution may be slightly acid, neutral or alkaline. HCl interferes most with complete separation, HNO_3 less, and H_2SO_4 least. If the solution is acid with any large proportion of these, the precipitation is best effected in the cold.

Sol.—Dissolved by dilute boiling HNO_3 , though that solvent almost invariably affords some PbSO_4 . Of concentrated acids hot HCl is the best solvent, since with either HNO_3 or H_2SO_4 some PbSO_4 will form in such a way as to protect a portion of the sulphide. Soluble in $\text{Na}_2\text{S}_2\text{O}_3$.

Ign.—Volatilized. Easily reduced to metal by ignition with C.

AgCl.

Rem.—For determination of Ag, usual precipitant HCl. For determination of Cl, usual precipitant, AgNO_3 . Separates most readily in presence of an excess of silver salts. Partially decomposed by heating with strong HNO_3 or H_2SO_4 . Darkens in strong daylight, more quickly in sunlight, but may become very dark without material loss of weight.

Cond.—Acid solution, absence of any notable quantities of alkaline chlorides or other alkaline salts.

Sol.—Partially dissolved by moderately strong and hot HCl or HNO_3 . Somewhat soluble in alkaline and alkaline earth chlorides and nitrates. Readily soluble in NH_4OH , in KCy and in $\text{Na}_2\text{S}_2\text{O}_3$. In the latter, less readily if the substance has been changed by light.

Ign.—Fuses at a low temperature (dull red) and volatilizes at a little higher temperature. Easily reduced to metal by strong heat, especially when mixed with Na_2CO_3 or C. On burning the filter paper (which should be separated from the precipitate), the ash should be treated with HNO_3 to obtain AgNO_3 , then a drop or two of HCl is added to restore AgCl, and the whole after drying cautiously heated to incipient fusion.

As₂S₃.

Rem.—Usually precipitated by H_2S in HCl acid solution. From the solution of arsenic sulphides in alkaline polysulphide, the addition of acid separates As_2S_3 . As_2S_3 requires very thorough drying before weighing, the last portions of water being driven out with difficulty.

Cond.—Solution acid, with some mineral acid (HCl preferable).

As should be in triad form. If in pentad form, it is slow to reduce and precipitate ($\text{As}_2\text{S}_5 + \text{S}_2$) by prolonged action of H_2S and warming.

Sol.—Dissolved by alkaline solutions (hydrates, carbonates or sulphides), also by aqua regia, fuming nitric acid, water solutions of chlorine, bromine, etc. In a neutral solution, scarcely any precipitation occurs. Insoluble in strong HCl even on boiling. Practically insoluble in H_2SO_4 . Dissolved by KHSO_4 .

Ign.—Readily volatilized without change of composition.



Rem.—Usual precipitant MgCl_2 in ammonia solution containing alcohol. Precipitate white, crystalline, closely resembling MgNH_4PO_4 .

Cond.—Solution alkaline with ammonia, containing a minimum amount of NH_4Cl , and 25 to 30 per cent. of alcohol. No sulphates or other compounds, partially or entirely insoluble in alcohol of this strength, should be present. The As must be in pentad form (a condition realized in solutions containing alkaline polysulphides).

Sol.—Dissolved by acids, or on application of heat. Somewhat soluble in water and in NH_4Cl , an effect partly neutralized by presence of ammonia and alcohol, in which it is insoluble.

Contam.—Basic Mg salts, sulphates and other salts partially or entirely insoluble in diluted alcohol.

Ign.—Partially volatilized if heated up quickly. By slow heating it is dried and finally altered to $\text{Mg}_3\text{As}_2\text{O}_7$, which is non-volatile. With C partly volatile. A convenient method of management consists in dissolving the washed precipitate through the filter by dilute HNO_3 into a weighed capsule, evaporating, igniting slowly and finally intensely.



Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of sulphantimonite.

On drying, the precipitate does not surrender all H_2O until the temperature is raised to 200°C when it becomes black. This degree of heat is liable to char the paper when dried on a weighed filter.

By the action of oxidizing agents (Br , HNO_3 , HgO , etc.) it is converted to Sb_2O_3 .

Cond.—Solution slightly acid and moderately dilute. An excess of H_2S causes a more rapid separation of the precipitate. If too acid or too concentrated the precipitation may be imperfect.

Sol.—Precipitate dissolved or prevented from forming by moderately concentrated acids, especially HCl . H_2SO_4 has much less effect. The preventive effect is increased with the temperature. Tartaric acid in the solution assists precipitation.

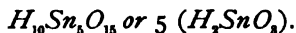
Dissolved by fixed alkalis or alkaline sulphides.

Scarcely soluble in ammonium carbonate or $KHSO_4$.

Somewhat soluble in $H_2C_2O_4$, but insoluble in it if boiled in presence of an excess of H_2S . (Separation from tin.)

Contam.—S usually accompanies the precipitate. To remove this the water is first displaced by alcohol, and the S dissolved out by CS_2 .

Ign.—Partially or entirely volatilized by ignition alone, or with reducing agents. Mixed with 30 to 50 times its weight of HgO and ignited, it is converted to Sb_2O_3 , which is stable at the ordinary temperature of ignition. Frequently, however, it is converted to Sb_2O_3 by Br or HNO_3 before ignition.



Rem.—The above is called the "insoluble" form of hydrated stannic oxide, because not readily soluble. It is usually obtained by boiling slightly acid (HNO_3 or H_2SO_4) solutions containing the soluble form in partial suspension, or by boiling weakly acid solutions (of stannic compounds) containing neutral alkaline salts (NH_4NO_3 , $NaNO_3$, Na_2SO_4 , etc.). The presence of acetates assists the separation.

Cond.— HCl or chlorides should be small in amount, preferably entirely absent. Solution should be acid, tolerably dilute, and boiled for some time.

Sol.—The "soluble" form (obtained by neutralizing stannic solutions with caustic or carbonated fixed alkalis) is readily soluble in excess of the alkali or in acids. The "insoluble" form is only soluble with difficulty in HCl , or in caustic alkali, and practically insoluble in dilute HNO_3 or H_2SO_4 .

Contam.—As and Sb oxides, which should have been removed previously. In analyses of bronzes, etc., CuO removed by long digestion with dilute HNO_3 . SiO_2 removable by treatment with

HF and H_2SO_4 . Fe_2O_3 , removed by fusion with NaOH or Na_2CO_3 , and after further treatment by well-known methods, separating the Fe_2O_3 , which is weighed and deducted. This operation is usually performed upon a *weighed portion* of the precipitate.

Ign.—Requires intense heating to remove all H_2O . Not easily reduced to (volatile) Sn by C , though such reduction is possible, on igniting the precipitate. Volatilized as chloride by ignition with NH_4Cl . Otherwise not volatile at high temperatures.

SnS_2 .

Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of alkaline sulpho-stannate. Obtained for purposes of separation, or for determination as SnO_2 after oxidizing. Disposition to run through the filter checked by alkaline acetates or nitrates, etc.

Cond.—Solution slightly acid, moderately dilute. Precipitation promoted by acetates, interfered with by alkaline oxalates or oxalic acid.

Sol.—Moderately concentrated acids, especially HCl , dissolve or prevent precipitation. The influence is more marked the more concentrated the acid, or the higher the temperature. Soluble in a boiling solution containing free $\text{H}_2\text{C}_2\text{O}_4$. (Separation from Sb .)

Ign.—If rapidly and strongly heated, some SnS_2 may be volatilized. By moderate heating with access of air, SnO_2 forms without loss. It is, however, usual to assist the oxidation with a few drops of HNO_3 added from time to time.

Ammonium Phosphomolybdate. $12\text{MoO}_3(\text{NH}_4)_3\text{PO}_4 +$.

Rem.—Yellow finely crystalline precipitate. Precipitant $(\text{NH}_4)_2\text{MoO}_4$ in HNO_3 solution. The ratio of MoO_3 to P_2O_5 in the precipitate varies according to the proportion of substances present in the solution (NH_4NO_3 , $\text{Fe}_2(\text{NO}_3)_6$, etc.), the proportion of free acid, the kind of acid, the length of time elapsing before filtering, and the temperature at which it is effected. With the same or closely similar conditions, the ratio of MoO_3 to P_2O_5 is essentially the same. Precipitation promoted by agitation. When precipitation is complete, the precipitate settles rapidly after stirring. Precipitated under the conditions described by Emmerton (volumetric determination of P in irons), the ratio of MoO_3 to P_2O_5 is 24 to 1.

Cond.—Solution should be acid with HNO_3 . Too much free HNO_3 retards or may prevent complete precipitation; too little allows Fe_2O_3 to come down with it, in which case the color is more orange. An excess of the precipitant should be present; also at least 10 gms. of NH_4NO_3 for every 0.1 gm. or less of P present. Temperature should be 70 to 85° C. Below 70° the separation is very slow, whereas on boiling (other conditions being right) MoO_3 or Fe_2O_3 may accompany the precipitate. Reducing agents, organic acids, silica, chlorides and HCl should be absent. H_2SO_4 and sulphates retard precipitation. If the precipitate is to be dissolved for volumetric estimation, in a solution of material containing but little iron, some iron should be added to give correct results, or the standard should be obtained with material of the same character.

Sol.—Readily dissolved by NH_4OH and other alkalies; also by alkaline phosphates. If the ammonia is too strong, however, the solution will be turbid with $(\text{NH}_4)_3\text{MoO}_4$. Dissolved or decomposed by water alone, the more readily the higher the temperature. Precipitation prevented by tartaric acid or organic substances of that class. Somewhat soluble in HCl , or moderately strong H_2SO_4 and HNO_3 . Insoluble in weakly acid solutions and acid solutions of NH_4 salts. Solution for washing should contain 1 per cent. HNO_3 and 10 per cent. NH_4NO_3 , or a corresponding amount of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.

Contam.—Arsenio-molybdate, silica, Fe_2O_3 , TiO_2 .

Arsenio-molybdate precipitates the less readily the lower the temperature. By allowing the solution to stand for about two days at 40° C., the phospho-molybdate may be precipitated free from arsenic. When present, however, As is separated either before or after.

Silica, either as hydrated SiO_2 or as silico-molybdate (the existence of which is disputed), may be present. By allowing the ammonia solution to stand for some time after addition of NH_4Cl , the flocculent silica separates and may be filtered off.

Fe_2O_3 in the precipitate often causes it to separate in crusts on the sides of the beaker. On attempting to dissolve in ammonia, yellow to red $\text{Fe}_2(\text{OH})_6$ mixed with $\text{Fe}_3(\text{PO}_4)_2$ remains undissolved. After washing with ammonia, this residue is dissolved in HNO_3 ,

the solutions united and reprecipitation effected, after acidifying with HNO_3 .

Hydrated TiO_2 (which retains P_2O_5) can be separated by fusing the portion insoluble in ammonia for some time with Na_2CO_3 (*vid.* Na_2TiO_2), leaching with water, and in the water solution reprecipitating with the molybdate reagent.

SILICA.

Rem. and Cond.—On adding an excess of mineral acid to a solution containing a silicate, free silicic acid containing indefinite amounts of water is formed, partially or entirely soluble. On evaporation H_2O (of constitution) is removed and insoluble SiO_2 is separated, which may be filtered off after digestion with diluted acid. HCl is the acid most frequently used. When HNO_3 is used, regard must be had to the fact that certain nitrates ($\text{Fe}_2(\text{NO}_3)_6$, etc.) are decomposed at the temperature usually employed to drive out the last portions of the water (110 to 130°C.), and are not readily re-formed by digestion with diluted HNO_3 . The heat is usually maintained until there is no perceptible odor of acid. With H_2SO_4 , the heat is continued until fumes of H_2SO_4 are evolved, indicating that H_2SO_4 is the only free acid remaining. If the heat has not been sufficiently prolonged or intense, the separated silica may be flocculent and filters with difficulty, or some may remain soluble.

If the heat has been too high, the conditions may have favored a re-combination of silica with the bases, and consequent soluble silica (analogous to the action by fusion). The temperature which can safely be applied may be put at 110° to 120° .

According to Gilbert (*Techn. Quarterly*, February, 1890; this Journal 4, 159), when only Ca and alkalies are present, the temperature of drying may be carried up to 280°C. without detriment, but if Mg is present, re-combination of the bases with the silica is best prevented by drying at 120°C. Some alumina almost invariably remains with the silica if Al is present in the solution.

Sol.—Dissolved by boiling or fusing with fixed alkalies, caustic or carbonated. Insoluble in water and acids (HF excepted).

Contam.—Insoluble sulphates (PbSO_4 , BaSO_4) removed by digestion with conc. H_2SO_4 , and filtering through asbestos. (For other solvents of these substances, *vid. sup.*) In some cases

CaSO_4 , removable by digestion with HCl and NH_4Cl . The precipitate may also contain a form of $\text{Fe}_2(\text{SO}_4)_3$ (when separated from conc. H_2SO_4) which dissolves in dilute H_2SO_4 with some difficulty, but is readily soluble in HCl .

SnO_2 or Sb_2O_3 may be retained, as well as TiO_2 (possibly combined with P_2O_5) and ferric or aluminic oxides or basic salts. TiO_2 tends to hold P_2O_5 , Al_2O_3 , and Fe_2O_3 in the precipitate. To avoid error in such cases, the SiO_2 should be determined by loss, adding HF or NH_4F (and in any case H_2SO_4) igniting to drive off SiF_4 and weighing again. This treatment is advisable whenever Al_2O_3 is present in the solution in any quantity.

Ign.—Precipitate is very light and fine, and readily carried off by flame, requiring especial precaution on igniting. After ignition, the precipitate will absorb appreciable amounts of water if exposed to air containing moisture.

NOTE UPON THE ESTIMATION OF MILK. SUGAR IN MILK.

BY AUGUSTUS H. GILL, PH.D.

The main difficulty in this determination, as ordinarily carried out, is in obtaining a filtrate sufficiently clear for titration; as prepared by the usual methods is opalescent or even quite turbid from the fat which passes through the filter.

It has been found that by making use of the well known property of aluminum hydrate to drag down precipitates, and by following the recommendations of Radlscu,* regarding the amount of acid, intensity and duration of heating, all of which are of great importance in the rapidity and completeness of the curdling, that a clear filtrate is readily obtained.

The method is as follows: 25 cc. of the milk are mixed with 15 cc. "milk of alumina," and 0.5 cc. of twenty-five per cent. acetic acid added, the mixture stirred, and heated 5-7 minutes in a water bath, the temperature of which is 85 degrees C. 100 cc. of water are now added, and the mixture is heated in boiling water for ten minutes, with frequent stirring. It is thoroughly cooled under the tap, allowed to settle, and decanted through a plaited

*Mittheilungen a. d. pharm. Inst. u. Labor. d. Univ. Erlangen, Hilger. Heft III, pp. 93-112.

filter (S. & S. No. 597) into the 500 cc. graduated flask, being careful to bring as little precipitate upon the filter as possible. The operations of boiling and filtering are repeated three times, and the filtrates made up to 500 cc. It is then ready for titration by Fehling's solution in the usual way.

The "milk of alumina" is prepared by precipitating at the boiling temperature 125 gms. ammonia alum with ammonium hydrate, washing the precipitate by decantation, and making it up to one liter.

The method has been in use by the students here for a year and given very satisfactory results.

MASS. INST. OF TECHNOLOGY, BOSTON.

LABORATORY OF SANITARY CHEMISTRY.

THE NICKEL MINES OF NEW CALEDONIA.*

REPORT BY VICE-COMMERCIAL AGENT LEMESCAM, OF NOUMEA.

It has come to my knowledge that several European governments have been making inquiries here concerning the production of nickel ore in this country, and I deem it my duty to make a report on the subject to the Department.

The area of New Caledonia is 2,000,000 square kilometers, and it includes about 800,000 square kilometers of nickel-producing land. About 80,000 square kilometers have already been granted to, or applied for by, divers mining companies, but about 20,000 square kilometers of the land are being actually worked, principally in districts easily reached by sea or rivers. Some of the best claims are not yet worked on account of the difficulties resulting from the absence of roads.

The composition of the nickel ore is hydrated silicate of nickel and magnesia, without any traces of arsenic. It contains from 8 to 10 per cent. of metal, some samples containing up to 16 per cent. of pure nickel.

The value of 8 per cent. ore at shipping places is now 100 francs (\$19.03) per ton,† but the price will probably augment. The mines are reported to be inexhaustible.

Besides at Nouméa, ships can load at several other ports on

*From Consular Reports, July, 1891.

†The ton used in this report is equal to 1000 kilograms, or 2240 pounds.

each of the coasts of the colony, but foreign vessels have to pay coasting duties of 150 francs per registered ton at any other port except Nouméa.

Vessels coming to Nouméa with loads of lumber from the Pacific coast could get return cargoes of ore and save an expensive voyage to Australian ports. The exportation of ore from New Caledonia during the year 1890 has been: Nickel ore, 5000 tons; chromate of iron, 1500 tons; cobalt, 700 tons; gold quartz, 10 tons; and of smaller metals—nickel, 1.50 tons; silver lead, 3.50 tons; copper, 1.32 tons.

The exportation will greatly augment henceforth, for large orders have been received by the Compagnie le Nickel for ore and metal. The Creusot foundries of France alone have ordered 100,000 tons of nickel ore.

Important foundries and furnaces are now being erected in the vicinity of Nouméa for the treatment of nickel ore, and the prospects seem to indicate that at a date not far off this colony will greatly surpass any country in the world in richness and importance of the nickel industry.

UNITED STATES COMMERCIAL AGENCY,
NOUMÉA, February 13, 1891.

TIN-MINING IN THE STRAITS SETTLEMENTS.*

REPORT BY CONSUL WILDMAN, OF SINGAPORE.

The passage of the new tariff law, which placed a duty on tin plate, has had a beneficial effect on the tin-mining of the Malay Peninsula insomuch as it increased the demand for pig tin in the United States. Formerly the tin that was destined for tin plate to be used in the United States was shipped in large quantities to different parts of the United Kingdom, where it was manufactured into tin plate and the plate exported to the United States instead of the raw material.

With the duty on tin plate this industry became less profitable to the English manufacturer, and, instead of shipping the manufactured article, the export of pig tin direct has in a great measure taken its place. In other words, pig tin is now going direct to the United States instead of by the way of Great Britain.

*From Consular Reports, July, 1891.

According to statements made by the governor of the Straits Settlements, this consular district mines half of the tin of the world. The export of tin from the Straits Settlements to all countries for the year 1889 amounted to \$23,254,023.

The mining of tin forms one of the chief industries of this peninsula, and is carried on principally in the native state of Perak, north of Singapore. The mining is done almost entirely by the Chinese.

The mining is that of flood tin, not rock, and this means that it is taken from the lowlands near the mountains, where it is found in seams or pockets 10 to 20 feet or more below the surface level in the shape of, or appearing like, coarse black sand, with here and there a mixture of tin and small particles of gold (dust). To get at the placer tin means a great upheaval of soil, pumping of water from the pits, the washing of the exhumed stream tin, and the smelting of the latter. In most places the pumps, washing apparatus, and smelting furnaces are of the most primitive and simple, yet ingenious, character. The ore is smelted into slabs of irregular shape at the mines and sent to Penang and Singapore to be resmelted into marketable slabs or blocks and, at the same time, purified, and then shipped.

The tools used by the natives are very poor and simple, consisting of only a common hoe and a small, flat cane basket. With these the whole of the work is done. A basket, when full, holds about 4 pounds of earth. One of these baskets is placed at either end of a stout bamboo pole, balanced over a laborer's shoulders, carried off, and emptied, while the men with the hoe scrape together more soil and fill other baskets. The washing of the tin is done much in the same manner as our early miners washed for gold dust. The ore is found in Laroot (Perak) in large quantities in a stratum of whitish clay, which is washed in long open troughs, water passing through it, carrying off the soil, leaving the ore lodged against cleats nailed on the bottom of the trough.

The English and German companies now engaged in tin-mining do not take the trouble to smelt the ore at the mines, but ship the sand to Singapore, where large smelteries have been erected.

The price of tin has been quite firm since the passage of the new

tariff law, fluctuating slightly between about \$31.25 in August, 1890, and \$35.80, the present price, per picul (133 $\frac{1}{3}$ pounds).

The quantity and value of tin from the Straits Settlements that finds its way to the United States can hardly be correctly ascertained by the quarterly reports of the colony; for, as I have before pointed out, large quantities of tin, as well as other products destined for the United States, are shipped via London and Hongkong for reshipment, and consequently are not placed to the credit of the United States. However, the tin that went direct to the United States for the quarter ending September 30, 1890, amounted to \$1,157,323, against \$4,621,326 credited to the rest of the world, while for the quarter ended December 31, 1890, it amounted to \$1,217,930 (an increase of \$60,607 over the preceding quarter), against \$5,626,009 credited to the rest of the world, of which \$2,306,921 went to the United Kingdom.

About one-tenth of the carrying of tin between this port and the United States is done in American bottoms. The firms shipping from here are English and German. There is no American capital engaged in the production or exportation of tin, although the United States is such a heavy buyer.

In my judgment, if an American house were to be established in Singapore, it would control at once not only all the shipments of tin to the United States, but the shipment of nearly all of the \$11,000,000 of exports from the Straits Settlements to the United States.

UNITED STATES CONSULATE,
SINGAPORE, May 12, 1891.

NEW INDICATOR FOR ALKALIMETRIC DETERMINATIONS.

The fact that sulphur will be precipitated from its solution by contact with acid is the base of the author's idea.

The indicator consists of a concentrated solution of flowers of sulphur in an alkaline sulphide. The solution must be concentrated so as to bring the greatest amount of dissolved sulphur into the solution to be titrated without adding too much of the alkaline sulphide. What will adhere to a glass rod when dipped into the indicator is sufficient for a solution of 250 cc.—*W. Bolton, Ztschr. angew. Chem., 1891, 492.*

J. E. W.

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Oxygen and Nitrogen.—Leduc (Compt. Rend. 113, 186) has redetermined the specific gravity of these gases, and also of hydrogen. The data so far given are as follows, with air as unity :

<i>H.</i>	<i>N.</i>	<i>O.</i>
0.06947 } three	0.9719 } extremes	1.10501 } extremes
0.06949 } series.	0.9721 } of nine.	1.10516 } of three.
0.06947 }	0.97203 in mean.	1.10506 in mean.

Hence, when $H=1$, $N=13.99$, and $O=15.905$. The last figure should be corrected by the latest data as to the composition of water by volume, which would bring it down approximately to 15.903. The full details of the determinations are yet to be published.

Cobalt.—Hugo Remmler has studied the atomic weight of this metal from a new point of view.* Adopting the supposition of Krüss, that cobalt is composite in its nature, he infers that the discordance between the hitherto published determinations may be due to differences in the supposed elementary material itself, and then seeks for an experimental verification of the hypothesis. Finding that cobaltic hydroxide dissolves very slowly in aqueous ammonia, he prepared a large quantity of that substance, and made from it 25 ammoniacal extracts or successive fractions. These fractions were afterwards treated exactly alike, the cobalt in them being separated and purified, then converted into CoO , and the latter reduced by heating in pure hydrogen. Rejecting the first fraction, the remaining 24 gave him the following values for the atomic weight of cobalt, when $O=15.96$:

2. 59.531	10. 58.299	18. 58.519
3. 58.793	11. 58.372	19. 58.528
4. 58.934	12. 58.600	20. 58.652
5. 58.784	13. 58.514	21. 58.771
6. 58.722	14. 58.652	22. 58.778
7. 58.670	15. 58.831	23. 58.441
8. 58.384	16. 58.794	24. 58.535
9. 58.478	17. 58.858	25. 58.480

In the differences here manifested between the separate fractions, amounting in the extreme to nearly $1\frac{1}{4}$ units, Remmler finds evi-

*Untersuchungen über Kobalt. Erlangen Doctoral Dissertation, 1891.

dence for belief in the composite nature of cobalt. Repeated observations upon a single fraction gave him concordant values for the atomic weight, and hence he regards the variations indicated above as not due to experimental errors. It must be noted, however, that the tabulated values do not vary in any regular way, but that high and low are distributed quite unsystematically. Furthermore, the quantities of cobalt oxide reduced to metal in each experiment range from 0.099378 to 2.00259 gms., less than 1 gm. having been usually taken. As a rule, the amount of material used for each determination was much less than is commonly considered necessary for good measurements. The work is highly suggestive, but a careful repetition of it is certainly to be desired.

Copper.—T. W. Richards, continuing his researches upon the atomic weight of copper, has sought to discover the cause of the discrepancies between his earlier results (63.6) and the value found by Hampe (63.32–63.34). The paper, which is admirably complete and thorough, a model investigation, is, however, too complex and elaborate for abstraction. Only the results can be given here. Hampe, in his work, depended upon the electrolysis of “anhydrous” CuSO_4 and of CuO . The former salt, as used by Hampe, is shown by Richards to have retained traces of water. The oxide was vitiated by occluded gases. Richard’s final results, including his earlier measurements, are tabulated as follows: The figures depending upon $\text{O}=16$, $\text{Ba}=137.10$, $\text{Br}=79.955$, $\text{C}=12.002$, $\text{H}=1.008$, $\text{Ag}=107.93$, $\text{Na}=23.053$, and $\text{S}=32.06$.

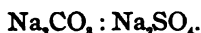
1. $2\text{Ag} : \text{Cu}$,	11 determinations,	63.601
2. $2\text{AgBr} : \text{CuBr}_2$,	3 “	63.609
3. $2\text{Ag} : \text{CuBr}_2$,	3 “	63.605
4. $(\text{CuSO}_4 - \text{Cu}) : \text{Cu}$,	3 “	63.593
5. $\text{Na}_2\text{CO}_3 : \text{Cu}$,	7 “	63.600
6. $\text{Na}_2\text{SO}_4 : \text{Cu}$,	4 “	63.607
7. $\text{Na}_2\text{CO}_3 : (\text{CuSO}_4 - \text{SO}_4)$,	2 “	63.621
8. $\text{Na}_2\text{SO}_4 : (\text{CuSO}_4 - \text{SO}_4)$,	3 “	63.641
9. $\text{BaSO}_4 : \text{Cu}$,	1 “	63.603
10. $\text{BaSO}_4 : (\text{CuSO}_4 - \text{SO}_4)$,	1 “	63.625
11. $(\text{CuO} - \text{Cu}) : \text{Cu}$,	5 “	63.604
General mean, eleven series		63.610
“ “ forty-three determinations,		63.606

Of these, ratios 1, 2, 3, 5, and 6 are regarded as the best, giving a mean of

$$\text{Cu} = 63.604,$$

which is to be taken as the final result.

Incidentally to this work, Mr. Richards determined the ratio



Eight experiments give in average a molecular weight for Na_2SO_4 of 142.169, when $\text{Na}_2\text{CO}_3 = 106.108$. Hence $S = 32.063$. Rejecting three of the experiments as less trustworthy than the others, he finds $S = 32.075$.—*Proc. Amer. Acad.* 26, 240.

Samarium—Bettendorff redetermines the atomic weight of samarium by the conversion of Sm_2O_3 into $\text{Sm}_2(\text{SO}_4)_3$.

1.0467	Sm_2O_3	gave	1.7675	$\text{Sm}_2(\text{SO}_4)_3$
1.0555	"	"	1.7818	"
1.0195	"	"	1.7210	"

$$\begin{aligned} \text{Hence, when } \text{O} &= 15.96, \text{ and } S = 31.98, \\ \text{Sm} &= 150.09; \end{aligned}$$

a result near the values found by Cleve and by Brauner (*Liebigs Annalen*, 263, 164).

QUANTITATIVE SEPARATION OF MANGANESE AND ZINC.

A mixture of 0.5 gm. manganese sulphate and 0.5 gm. zinc sulphate were dissolved in 75–100 cc. of water in a porcelain capsule (600 cc. capacity), and the solution was acidulated with hydrochloric acid. About 100 cc. of a 15–20 per cent. sal-ammoniac solution was added, then 60–100 cc. strong ammonia. No brownish coloration of manganese hydroxide must appear at this stage. 50–60 cc. of pure hydrogen peroxide were then poured into the solution, thoroughly stirred, and the manganese was completely precipitated. After heating on the water-bath for 10–15 minutes, the precipitate was filtered, washed with boiling water, slightly ammoniacal, and ignited over the blast lamp to a constant weight. The zinc in the filtrate may be determined by precipitating, first, as sulphide, then as carbonate, or by a method described as follows: The zinc solution is evaporated to dryness in a platinum

capsule on the water-bath, the resultant saline mass is heated at 125–150 degrees for one hour in an air-bath, and the ammoniacal salts are expelled completely by heating over flame, the capsule being protected by some asbestos from the naked flame. The residue is then dissolved in hot water, and a few drops of hydrochloric acid, filtered, and the zinc is precipitated in the filtrate with sodium carbonate.—*Paul Jannasch and J. F. McGregory, Chem. News 64, 182 (Journal für prakt. Chemie).* A. H. W.

NEW BOOKS.

Sadtler's Industrial Organic Chemistry.*—The chapter headings give a good idea of the subjects treated of. These are : 1, Petroleum and Mineral Oil Industry. 2, Industry of the Fats and Fatty Oils. 3, Industry of the Essential Oils and Resins. 4, The Cane Sugar Industry. 5, The Industries of Starch and its Alteration Products. 6, Fermentation Industries. 7, Milk Industries. 8, Vegetable Textile Fibres. 9, Textile Fibres of Animal Origin. 10, Animal Tissues and their Products. 11, Industries based upon Destructive Distillation. 12, The Artificial Coloring Matters. 13, Natural Dye Colors. 14, Bleaching, Dyeing, and Textile Printing. 15, Appendix. Each chapter begins with a description of the raw materials. Then the processes of treatment are taken up. Next the Products obtained are described and analyses given. Then the Analytical Tests and Methods are described, concluding with the Bibliography and Statistics.

The plan of the work includes too much material to allow of exhaustive treatment, but so far as it goes it is well planned and bears evidence of care in preparation.

The book is so good that it would be ungracious to speak in detail of the errors, mostly of omission, that are to be noticed here and there. The sections on Bibliography and Statistics add greatly to the value of the work, and for the student are invaluable. There are 127 illustrations, most of them good ones, and the paper and printing are good.

*A Hand-book of Industrial Organic Chemistry Adapted for the use of Manufacturers, Chemists, and all interested in the Utilization of Organic Materials in the Industrial Arts. By Samuel P. Sadtler, Ph.D. Philadelphia : J. B. Lippincott Co. 1891. 8vo., pp. xiv, 519.

THE
Journal of Analytical AND Applied Chemistry.

PYRITES AS A MATERIAL FOR THE MANUFACTURE
OF SULPHURIC ACID.

BY WM. H. ADAMS, M.E.

[Continued from page 615.]

It would seem, therefore, that no real benefit, in a money sense, need be expected from the development of the sulphur beds in this country, unless there is to be a radical depreciation in prices due to the solving of the chemical problems connected with alkali waste. It may be asked how this production can be hereafter guaranteed at prices which will lower the prices of Sicily or other products?

Sicily has now arrived at her maximum of production, or perhaps it might better be stated that she is at present supplying all the brimstone which the trade of the world within her reach demands—less than 400,000 tons annually,—and that cost prices for same will average a minimum of \$18.50 delivered in Europe or America.

Her sales during the past ten years have been in the ratio of—United States, 31 per cent.; France, 22 per cent.; Italy, 15 per cent.; Great Britain, 13 per cent.; other countries, 19 per cent. What would be the effect on this industry if the chemical processes of Europe produce from alkali waste 100,000 tons sulphur annually, or if domestic sources of supply should enable us to reduce the importations into America one-half, i. e., 50,000 tons?

It is well known that we are consumers of about 120,000 tons

of sulphur now, but a change in trade may be but a few years off, and either of the above, as established facts, are sure to bankrupt all the weaker companies in Sicily, which in turn will depress the price of brimstone below the cost of production. Such a state of affairs has occurred several times during late years, and only by concentration of stocks in stronger hands, renewal of works with more modern processes, increased and cheapened transportation and lessening the number of mines worked, has the industry been kept alive. With products of like character and value pressed for sale at figures below \$17, the result can only be disastrous to Sicily, while unsettling for a time our own industries where cost of raw materials are so largely the factors of success or failure.

As proof positive that the recovery process is thought to be successful in Europe, and therefore soon to be a disturbing element in trade, it may be stated that several firms have been offered a reduction of $33\frac{1}{3}$ per cent. on all future purchases of pyrites so long as they continue to consume the contract tonnage.

This means that all the pure sulphur as recovered from waste is to be forced for sale elsewhere, and not to be used in Great Britain; but shall take the place of imported brimstone, to the amount of 50,000 tons annually, and no more. Spanish pyrites sell in Great Britain for 4*d.* to 5*d.* per unit of sulphur, equivalent to \$3.60 to \$4.80 per ton of ore. These ores average 48 per cent. sulphur, therefore, after all losses are provided for, two and one-quarter tons of ore are equal to one ton of brimstone in acid manufacture. The cost of one ton of sulphur from ores is thus, from \$8.50 to \$11, while from brimstone it is not less than \$18.50, as stated.

Now, if from the present price, or cost of sulphur in ores, say an average of \$10, we deduct the concession offered to those manufacturers controlling or interested in the patents for recovered sulphur, and \$10 less $33\frac{1}{3}$ per cent. equal \$6.66 per ton of sulphur in ores delivered at works in Great Britain. At such prices for sulphur there will be a revolution in several industries.

These features of a possible struggle for supremacy in sale of the large tonnage of brimstone can mean but one thing to the average manufacturer, and has been so understood for many years past by the larger chemical companies. It means the unsettling

of prices, which none of the new companies can afford to face ; and a state of affairs long expected and provided against by the older companies, as shown by their change in plant to accord with modern practice, with ores which can be obtained in regular quantities at fixed prices. To the isolated smaller chemical companies, the varying prices on a consumption of 2 or 3 tons brimstone daily matters little ; it is everything to the large companies with a consumption of 20 to 30 tons sulphur daily, and with contracts made under heavy forfeits, for regular delivery of millions of pounds of acids.

The question of the purity of acids often arises in trade where sharp competition exists, but while it is positively necessary to have acids free from arsenic, selenium, etc., for some classes of trade, yet it requires no argument to prove that probably 96 per cent. of the trade of the world is suited with acids manufactured in the ordinary manner from pyrites. It is as simple a process to rectify pyrites acid, where the trade demands a perfectly pure acid, as any other step in a large business, and this special feature is now common to all well regulated chemical works.

We now turn to examine the inexhaustible deposits of sulphur ores which are so favorably distributed for use, and from which deposits in our own country there will gradually be developed industries in mining, milling, concentrating, chlorinating, acid making, and for treatment of residues.

Following absolutely in the old world paths, three of our best known chemical concerns commenced to work pyrites about the same time—1866-'68 : Watson & Clark, of Philadelphia, with the "Monnier process ;" Lodi Chemical Works, New Jersey, using the common type of English kiln, and the Phoenix Chemical Works, Brooklyn, N. Y., using the German shallow kiln. The former handled "fines" ores exclusively ; the latter firms only kiln-sized ores, but owing to irregularity of supplies of ores and the high price prevailing (\$8 to \$12 per ton of pyrites) their use was discontinued by 1869. Works at Boston, Mass., Bridgeport, Conn., and Anthony's Nose, N. Y., commenced working in 1869-'71, Canadian ores by the former and local deposits by the latter.

The sale of the Canadian mines to Scotch capitalists in 1874,

and the continued deterioration of the Anthony's Nose ores, caused a stoppage of these workings, and no further efforts were made to utilize pyrites until 1880, when ores from another Canadian mine were sent to New York in quantities.

Consumption of Pyrites in the United States.

	1881.	1882.	1883.	1884.	1885.	1886.	1887.	1888.	1889.	1890.	1891*
New York & vicinity,	7000	23900	29500	39000	44600	55700	59000	64000	72000	80000	160000
Boston & East. States,		2500	7500	14500	25800	26900	27000	30000	35000	40000	45000
Philadel'a & vicinity, . .		2500	5000	5500	11500	23600	25000	25000	28000	32000	50000
Baltimore & vicinity, . . .			2000	4000	7500	4300	5500	7000	12500	14000	14000
Southern States	1000	2000	3000	3000	3000	3000	3500	4500	7000	16000	26000
Western States			1000	2000	4000	5000	5000	10500	30000	40000	55000
Totals	8000	29900	48000	68000	96400	118500	125000	141000	184500	225000	290000

It should be stated that with old country experts in ore burning easily obtainable, there were good reasons for our tardiness in adopting the use of ores prior to 1880 :

1st. No mines were known or sufficiently developed, with transportation facilities, except those at Capelton, Canada, and those deposits were absorbed by the owners for copper purposes.

2d. Foreign ores (Spain, etc.) were excluded by reason of duties on iron and copper.

3d. The drawback to use of domestic ores was the 15 to 30 per cent "fines" which they invariably contained after long journeys, kilns being generally used for egg-sized ores, and no furnace had been successful for burning the "fines" (all that passed $\frac{3}{8}$ -inch mesh).

All these drawbacks have been overcome by experiments with every type of furnace and with the different classes of ores from all parts of the world ; demands for ores have been met by the development of the extensive deposits in New Hampshire, Massachusetts, Virginia,† etc.; and the working of both lump and fine ores are now so common as to deserve no special comment.

As the quality of the ores determine their value to a great extent, essentially so for acid making, a comparative table of the best known mine ores is herewith given, from which it will be seen that the United States does not fall below the average.

*Estimated in part, but will be over this tonnage rather than under for 1891.

†Trans. Am. Inst. Min. Engrs., 12, 527.

Composition of the World's Pyrites.

Localities.	Sulphur.	Iron.	Copper.	Zinc.	Lead.	Lime and		Arsenic.
						Magnesia.	Insol.	
English mines average	34.34	32.20	0.80	1.32	0.40	. .	30.00	0.91
French mines average	46.60	39.70	0.20	13.50	traces
German mines average	45.60	38.52	. .	6.00	0.74	. .	8.19	0.95
Belgian mines average	42.80	36.70	. .	0.40	0.92	5.45	12.47	0.20
Irish mines average	47.41	41.78	1.93	2.00	4.77	2.11
Swedish Mines Average	38.05	42.80	1.50	5.09	12.56	. .
Norwegian mines average	46.15	44.20	2.10	1.20	. .	2.50	3.65	traces
Arminius mines, Virginia	46.00	44.50	1.30	0.45	. .	1.32	4.32	none
Paulding County, Georgia	41.00	37.00	4.00	0.63	0.25	5.60	10.20	traces
Tallapoosa mine, Georgia	42.00	38.20	4.30	0.20	0.15	8.75	6.10	traces
Ducktown, Tennessee, average, .	35.00	58.00	2.50	3.40	1.10	0.40
North Carolina mines average . .	44.10	38.00	4.60	10.20	none
South Carolina mines average . .	45.20	40.40	3.05	10.15	none
Milan mines, New Hampshire . .	46.00	40.00	3.75	4.00	6.25	traces
Davis mines, Massachusetts . . .	46.00	42.00	1.55	2.10	8.60	traces
Elizabeth mines, Vermont	33.00	50.00	3.50	1.30	0.35	5.60	5.50	traces
St. Lawrence County, New York, . .	37.00	34.00	2.15	1.60	0.73	7.20	11.40	traces
Capelton mines, Canada	38.20	35.00	4.60	0.40	1.67	1.15	15.00	0.86
Rio Tinto mines, Spain	47.87	40.93	3.82	0.62	0.10	0.19	5.42	0.26
San Domingo, Portugal	46.00	43.50	3.15	0.15	0.45	1.30	5.10	0.15

THE GREAT SPANISH PYRITES DEPOSITS.

The mineralized zone of the Sierra Morena, in Andalusia, Spain, which is 160 miles long and 25 miles wide, is without question the grandest distribution of mineral wealth ever discovered. Exploited by the early Celts; extensively developed by the Phœnicians; and for three hundred years worked on the most gigantic scale by the Romans; with over 20,000,000 tons of slags and cinders visible to prove the activity and persistence of the ancients; with miles of underground workings, tools, timber and other evidences of their engineering and mechanical skill, we have in this section at the present time a series of object lessons in mining, mechanics, hydraulics and government beyond any comparison.

To the eastward are the rich lead mines of Linares; the Rio Tinto and Tharsus are in the center, and at the westerly end are the San Domingos group of mines in Portugal. Work was abandoned from the time the Moors obtained possession of the country until about 140 years ago, since which time mining has been carried on in a desultory manner, principally by the State, in order to support the resident population.

As the work produced no income over and above expenses, the Crown, for many reasons not necessary to mention, sold the prin-

cial mines to English capitalists, and workings were inaugurated by them on a scale befitting the magnitude and value of the deposits.

So many of the characteristic features of the district are met with in our own country, and, in fact, are common to most or all extensive deposits of pyrites, that a few sentences will sufficiently explain the resemblance geologically. The prevailing rocks are clay slates and crystalline slates, often highly metamorphosed. Parallel to the granitic tract of the Sierra, felsite, porphyry and quartzite have broken through the slates, and only in the neighborhood of such dykes are the beds of pyrites found. Their shape is that of large lenticular pockets in metamorphic clay slate from 100 to 500 feet thick, and extending 800 to 1,200 feet in length.

The whole bed is filled with pure pyrites, without appreciable gangue. These beds are found sometimes 12 feet below the surface, in a sandy condition, and easily gotten by pit work. In other places the zone of decomposition reaches from 60 to 300 feet below the surface.

It would require too much space to enumerate even the special features of interest connected with the work now going on along the range. Nearly three million tons of pyrites are raised from the mines each year, yielding over one million tons of sulphur and nearly one hundred thousand tons of copper. Of the copper about two-thirds, and of the sulphur perhaps two-fifths, are utilized by sale in the world's markets, the result being that by the opening of these mines, and the impetus given to trade generally, the price of the former has been reduced over one-half, and of the latter over seventy per centum since 1870.

There are three groups of mines well known to us, the Rio Tinto, the Tharsus and the San Domingos, but there are hundreds of lesser magnitude with ores of copper, manganese, lead, zinc blende, etc.; so that this mining section will continue to play a leading part in the history of chemical and metallurgical industries for many centuries to come.

The Rio Tinto mines are reached from the port of Huelva, South Spain, by a railway sixty-five miles in length. The deposits of this group are known as the North lode, the South lode, the San Dionisio lode and the Valley lode. The principal work-

ings are on the South lode, the openings being 4,500 feet in length, 300 feet in depth and 600 feet in width. To work this deposit advantageously it was decided to remove four and a-half million tons of surface earth, iron ores and granular pyrites too poor in copper to be worth saving. This done, 300 feet of clean quarry ores lie above the double-track tunnel, and lateral branches enables the entire mass of copper-bearing pyrites to be loaded from shutes directly into cars. 700,000 to 800,000 tons are thus taken from the South lode every year, and a fair estimate of the body of ore now disclosed above and below the tunnel is one hundred million tons. The tunnel which is now used for this work will eventually be driven three miles to reach the San Dionisio lode, the ore bodies of which are in excess of the South lode. Over one and a-half million tons are annually mined by this company, all of which is worked for copper alone on the ground, or shipped from Huelva to be worked for sulphur, copper, iron and precious metals. Naturally the plant of such a property must excite admiration. The railway is capable of transporting 2,000 tons daily to Huelva, where shipping facilities are on the same liberal scale.

The question of a sufficient water supply to continue throughout the year the operations of copper extraction by wet methods has now been solved by occupation of the Odill basin, and the impounding therein, behind a dam eighty feet high, of over one hundred million cubic feet of water. Cast iron pipes fifteen inches in diameter and nearly seven miles in length deliver this water to the different workings. The precipitating tanks for copper manufacture, if joined together, would be about seven miles long, and ore piles containing one hundred thousand tons of low grade copper ores undergoing leaching treatment are commonly met with, several million tons in all stages of working being constantly under supervision by the vast army of workmen.

The Tharsus mines* are second only to the Rio Tinto, with an output of one-half million tons annually, and the San Domingos rate as third, with over three hundred thousand tons output every year.

*The report of the Tharsus Sulphur and Copper Company shows that the total over-burden removed from the Tharsus mines for the year 1889 was 342,797 cubic meters, as against 197,974 in 1888. The mineral weighed 206,192 tons, against 382,109—a decrease of 85,917 tons, an increased proportion of the ore having again been taken from the Calanas mine. The mineral extracted from the Calanus and Tharsus mines for the year 1889 was 539,048 tons, as against 580,149 the previous year. The shipments for that year were 244,389 tons large, and 6,029 tons smalls—total, 250,418 tons.—*Eng. and Min. Journal*, May 10, 1890.

In addition to this enormous tonnage from Spain and Portugal, there is also mined in Ireland and England about 40,000 tons; in Germany about 150,000 tons; in France about 200,000 tons; in Belgium about 50,000 tons, all of which is consumed at home, and in Sweden about 30,000 tons for export. These amounts are consumed in addition to imports from Spain, as stated, making about two million tons of pyrites now utilized.

Products from Two Million Tons Spanish Ores, One Year's Output, at Present Prices.

Sulphur, 900,000 tons, market value, say \$15	\$13,500,000
Copper, 60,000 tons, market value, say \$200	12,000,000
Iron, 1,200,000 tons, market value, say \$3	3,600,000
Gold and silver.	2,000,000
Market value of mine products	\$31,100,000

While such a possibility as marketing the entire annual output of those mines is, of course, a remote one, yet who can say, in the light of operations for the past thirty years, what may not be done in the coming twenty or thirty years. If that class of mines were in our own country and worked on the scale of the Tharsus mines, say half a million tons yearly, we could soon absorb that tonnage, and at to-day's prices the results would be as follows:

Results of Mining and Working 500,000 Tons Pyrites in the United States.

Products—

Sulphur, average 45% = 225,000 tons, valued at \$10, \$2,250,000	
Copper, average 3.5% = 17,500 tons, valued at \$200, 3,500,000	
Iron residues, say 200,000 tons, valued at \$3	600,000
Gold and silver, valued at \$1	500,000
Total products	\$6,850,000

Costs—

Mining 500,000 tons at \$1.50	\$ 750,000
Freights to chemical works at \$2	1,000,000
Copper extraction 17,500 tons at \$80	1,400,000
Gold and silver extraction	200,000
Incidentals, interest, etc.	500,000
	3,850,000

Balance is annual net profit \$2,000,000
Or profit per ton of mine ore, \$4.

As the capital required for such an enterprise as the above would not exceed \$3,000,000, the results would be very satisfactory.

I introduce these statements principally to show the wide difference in values between the old-time methods of mining, strictly for sale of one product in the ores, and the new procedure by which capital is brought to bear to carry the ores through every stage of beneficiation. It is a well-known fact that all the pyrites ores sent to England and the Continent up to within a short time by the three large companies mentioned cost absolutely nothing as delivered to the extraction works, the sale of the sulphur under contract recouping them for outlay, as witness :

One ton Spanish ore sent to England contains average 46 per cent. sulphur, which is sold for 6d. per unit	\$5.50
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Costs on same to owners :

Mining	\$1.00
Freights to Huelva, rail	1.00
" England, vessel	3.25
Storage and delivery25 5.50

The result of so handsome a business operation as the securing of long-time contracts for supplies of sulphur in ores containing copper, is that the copper, iron and gold and silver is only chargeable with the small cost of extraction from materials almost fully prepared for such a process. But for the unforeseen supplies of copper from Montana and the extravagant expenditure in development of the Spanish mine deposits fifty years in advance of necessities, we should know them now as the largest and surest dividend payers in the world. As it is, however, the many chemical and metallurgical industries which have run along in grooves for ten years past, while sulphur in ores sold at 6d. per unit, will now have an awakening to newer life with sulphur offered from $1\frac{1}{2}d.$ to 4d., and it is such radical changes which, in America, we should watch and take advantage of. Germany has a way of altering her methods of manufacture when dissatisfied with fluctuations in prices of sulphur in Spanish ores. Thus, the Renania Chemical Works, as one example, have chambers at Stolberg,

Oberhausen, Hamhorn, Bensburg and Dortmund, in connection with and making use of the waste gases from zinc smelting works. 12,000 tons of 60 degree B acid were made by this company in 1880, while this year they will turn out over 80,000 tons of same grade acid, following the natural increase of trade without disturbing values, but freeing themselves from dictation of English sellers of pyrites.

As the waste gases of the Rhine and Westphalia zinc works are able to furnish double this amount of acid, preparations are now being made to insure a market for the surplus over and above natural necessities in manufacture of ammonia sulphates—taking waste gases from the coke ovens for source of nitrogen.

With regard to other deposits of pyrites in Europe, they are identical in so many respects, except as to magnitude, that we will pass them by at this time. Among them, however, the Mansfield copper-silver ores deserve mention at greater length than possible in this article. These mines are on the southern slope of the Hartz mountains in Northern Germany, between Sandersleben and Eisleben, although mines were formerly worked 30 miles southwest in the Thuringia mountains. 50,000 people are directly dependent upon the success of these mining operations, and 18,000 are actually employed in ore mines, coal mines, chemical and metallurgical works, and for the official staff. The income from all sources is about \$7,500,000, with expenses probably \$6,000,000. Among the items of manufacture in 1888 are copper, 12,000 tons, and silver, 80 tons. The total cost of ore delivered to works is over seven dollars per ton, even on an annual output of over 400,000 tons; the copper averages about 3 per cent., and the silver over 5 oz. per ton.

This magnificent enterprise stands without a rival among the copper companies of the world, inasmuch as so many auxiliary branches are successfully conducted from the mines' products, and is a fit type of diversified working eminently applicable to several sections of our own country.

[TO BE CONTINUED.]

XVII. THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

Up to within the last year, the estimation of iron and aluminum in the presence of large quantities of phosphoric acid has always been attended with great difficulties, it being impossible to obtain results which approximated to the actual amounts of these bases present, or even agreed among themselves.

It was in connection with some analyses of phosphatic rocks in the work of the Chemical Division of the Department of Agriculture that my attention was first drawn to this subject last spring, and I was directed by the chemist to make a thorough study of all the methods proposed for this work. In the following paper is found a resumé of the work which I have done in this line. I will first give an abstract of the various methods which have been proposed.

The one which has been most generally used, and which is at the same time the most inaccurate, is conducted as follows :

200 cc. of a hydrochloric acid solution (= 4 gms. material) are taken, and ammonia added to alkaline reaction. Care must be exercised not to add too great an excess, or time will be wasted in boiling it out. The ammonia precipitates the iron and aluminum together with the phosphoric acid. Boil the solution until the vapors are no longer ammoniacal. Allow the precipitate to settle, and decant the clear fluid on a filter. Wash with 50 cc. of boiling water, stir, allow to settle and decant as before. As some lime and magnesia may be carried down, dissolve in the beaker with as little hydrochloric acid as possible and reprecipitate with ammonia, boiling as before. Wash by decantation 3 or 4 times, using 50 cc. of boiling water each time. Finally transfer to the filter with boiling water, wash free from chlorides, dry in air-bath at 110 degrees C., ignite gently until the paper is burnt, then heat intensely, cool and weigh.

The weight of phosphoric acid in this precipitate is found by any of the usual methods, preferably the molybdate method, and

*Read before the Washington Chemical Society, Nov. 12, 1891.

is deducted from the total weight, the oxides of iron and aluminum being thus found by difference.

Several methods have been elaborated which are based on the previous separation of the phosphoric acid. One of the first of these is that of Sonnenschein.

This method is applicable to all cases in which the phosphoric acid is present as orthophosphoric. The material is dissolved in dilute nitric acid and sufficient molybdenum solution added to precipitate all of the phosphoric acid. The precipitate of ammonium phosphomolybdate is filtered off and washed with a dilute solution of ammonium nitrate. A sufficient excess of ammonium sulphide is added to the filtrate, the molybdenum sulphide is removed by filtration and the bases separated in the filtrate by means of ammonium hydrate.

This method should theoretically give correct and accurate results, but up to this time it has never been generally used, various analysts reporting their inability to obtain good results. The causes of the failure have never been satisfactorily explained.

Stutzer proposed the following method :

Precipitate the iron and aluminum as phosphates by means of ammonia, collect on a filter and wash once with water, then transfer filter and precipitate to a beaker and add 150 cc. of molybdate solution to cause the separation of the phosphoric acid. Filter and precipitate the bases in the filtrate by means of ammonium hydrate.

This method should also give good results, but it has been discarded, as in some inexplicable manner it would at times suddenly fail.

Dr. J. H. Vogel has investigated Stutzer's method very thoroughly, and takes the following exceptions to it: That the addition of such a large amount of molybdate solution is not at all justified, and renders subsequent operations difficult, there being present 75 cc. of concentrated nitric acid, which must be neutralized before the hydrates can be precipitated with ammonia. The presence of the filter also renders the washing of the precipitate difficult and necessitates a large amount of wash water. He has, therefore, modified the method as follows: The precipitate of iron and aluminum phosphates is collected on a small filter. It is not

washed, and in case the last drops of filtrate do not come through rapidly it is not necessary to wait, but the precipitate may be immediately dissolved, as small quantities of the filtrate do not change the results. The first precipitation of the phosphates by ammonia according to Glaser (see description of this method) only serve the purpose of removing the bulk of the phosphoric acid, as its presence would necessitate the use of very large quantities of the molybdate solution, and it is on the other hand necessary to work with small and concentrated amounts of the liquid. In all his experiments, Dr. Vogel found that 50 cc. of molybdate solution were sufficient. This amount, however, is regulated by the quantity of the precipitate which we have, and must be left to the judgment of the analyst. The 50 cc. of the molybdate solution are put into a 100 cc. graduated flask, and about 30 cc. poured on the precipitate. The strong nitric acid present immediately dissolves the latter. The filter is then washed with the other 20 cc. which have previously been diluted to 100 cc. 100 cc. are always sufficient for washing and we need not consider any yellow color present on the filter, as the acid wash water will rapidly remove all the bases. The filtrate and washings are allowed to stand until the phosphoric acid is completely precipitated. The whole liquid is then transferred to a filter and the beaker washed three or four times with a solution of ammonium nitrate, the filter being washed an equal number of times. The filtrate containing the bases is then rendered strongly alkaline with ammonia, and the liquid brought to the boiling point. It is not necessary to expel the excess of ammonia, as the large amount of ammonia salts present prevents any solution of alumina or precipitation of magnesia. By proceeding in this manner we get a precipitate free from molybdic acid, unless we are working with very large amounts of iron and alumina, in which case the hydrates must be dissolved in dilute hydrochloric acid and reprecipitated with ammonia.

I now come to another modification of the molybdate method which I have used with perfect success and which has invariably given accurate results, both to me and to several other assistants in our laboratory. This modification was first used in this laboratory by Mr. K. P. McElroy, for the estimation of alumina in phosphatic baking powders.

100 cc. (= 1 gm. substance) of a nitric acid solution of the substance are placed in a 500 cc. flask, and a solution of ammonium molybdate added until all of the phosphoric acid has been precipitated. The addition of ammonium nitrate will hasten the separation of the ammonium phosphomolybdate. It is best to let the liquid stand over night. It is then made up to the mark, filtered through a dry filter, and duplicate samples of 200 cc. each of the filtrate taken for analysis. A small quantity of ammonium nitrate is dissolved in the liquid and ammonia cautiously added, keeping the solution as cool as possible. The iron and aluminum will come down as hydrates. They are collected on a filter and washed with water, the filtrate and washings being collected in a beaker. It is usually best to redissolve the precipitate with a few cc. of a solution of ammonium nitrate in dilute nitric acid, reprecipitate with ammonia, filter, wash, ignite and weigh. This excludes all possibility of error by the presence of molybdic anhydride. After weighing, the oxides may be fused with sodium bisulphate, dissolved in water and the iron determined volumetrically in the usual manner. My results on as small quantities of material as .200 gm. have always been closely concordant. I usually take four portions of 100 cc. each (= .200 gm.); in two of these I determine both oxides gravimetrically, and in the other two I redissolve the freshly reprecipitated hydrates in dilute sulphuric acid and determine the iron volumetrically.

This method may be expanded as proposed by Mr. McElroy, so as to permit the estimation of other bases in the same portion of the material. For this purpose the filtrate and washings from the first precipitation are collected. Sufficient ammonium oxalate is added to them to precipitate the calcium. As the ammoniacal solution must be kept cool, this precipitate is very fine, and I have found that the only way to collect it satisfactorily is by using a Gooch crucible without pressure. By proper packing of the asbestos film, the filtration can be made quite rapid and satisfactory. The filtrate and washings are again collected and a solution of sodium phosphate added to precipitate the magnesia. It is absolutely necessary to keep all solutions cold and ammoniacal during these operations so as to prevent the separation of molybdic anhydride.

Of the methods lately proposed for the determination of iron and aluminum in phosphates the most prominent is the method of Glaser, also called the "alcohol method."*

Glaser proceeds as follows:

5 gms. of the phosphate are dissolved in the usual manner in 25 cc. nitric acid (sp. gr. 1.20) and 12.5 cc. of hydrochloric acid (sp. gr. 1.20) and made up to 500 cc. 100 cc. of the filtrate are placed in a 250 cc. flask with the addition of 25 cc. of sulphuric acid (sp. gr. 1.84.) The flask is allowed to stand for 5 minutes, shaking occasionally. About 100 cc. of 95 per cent. alcohol are added, the flask is cooled, made up to the mark with alcohol and well shaken. After standing one-half hour the liquid is filtered. 100 cc. of the filtrate (= 0.4 gm.) are evaporated down in a platinum capsule until the alcohol is expelled. The residual solution is mixed with 50 cc. water in a beaker and brought to a boil. Ammonia is then added to the solution until the reaction is alkaline, but not whilst boiling, to avoid violent effervescence. The excess of ammonia is removed by boiling, the solution is allowed to cool, filtered, the precipitate washed with hot water, ignited and weighed as ferric and aluminic phosphates.

Jonest† investigated Glaser's method and found that—

a. The amount of alcohol prescribed was not sufficient to precipitate all the calcium sulphate.

b. The amount of sulphuric acid is much more than is actually necessary.

He therefore modified the method as follows:

10 gms. of the substance are dissolved in nitro-hydrochloric acid and the solution made up to 500 cc. 50 cc. of this solution (= 1.0 gm.) are evaporated down to 25 cc. and whilst hot, 10 cc. of dilute sulphuric acid (1:5) added, the whole stirred and cooled. 150 cc. of 95 per cent. alcohol are then added, and after stirring, the solution is allowed to stand three hours. The calcium sulphate is then collected on a filter, washed with alcohol, and the filtrate and washings collected in an Erlenmeyer flask. The washing is complete when the last 10 drops after dilution with an equal volume of water are not colored red with a drop of methyl-orange.

*Chem. News, 63, p. 146.

†Zeitschr. f. angew. Chem., 1891, No. 1, p. 3.

The calcium sulphate whilst moist is transferred to a platinum crucible, the filter placed on it, the alcohol burnt off and the filter incinerated. The calcium sulphate is then ignited and weighed. The contents of the flask are heated to expel the alcohol, the residue washed into a beaker, made slightly alkaline with ammonia and again heated until all the ammonia is driven off. This is absolutely necessary, as otherwise the precipitate will be contaminated with magnesia. The precipitate is collected on a filter, washed four times with hot water or water containing ammonium nitrate, dried, ignited, and weighed.

An excess of ammonia is added to the filtrate and washings, the whole allowed to stand 12 hours, when the magnesia will have separated as ammonium-magnesium-phosphate, which can be collected, ignited and weighed as usual.

Immediately after the above methods were published, considerable discussion arose with regard to the presence of magnesia in the precipitate of iron and aluminum phosphates.

Theodor Meyer* states that unless all of the ammonia is driven off, the precipitate will contain magnesia, and on the other hand continued boiling not only drives off the free ammonia, but also some of the combined, forming acid ammonium sulphate, which redissolves some of the precipitate. This, however, separates out again on standing.

K. Wohlrab† and von Gruber,‡ however, dispute Meyer's statement, reporting analyses of known mixtures.

It does seem improbable that during the short time which is required for the precipitation any appreciable quantities of magnesia could separate.

At one of the last meetings of the Chemical Manure Manufacturers' Association, the following exceptions were taken to the original Glaser method and the following modification adopted.§

Exception made :

a. To working upon a solution representing so little as 0.4 gm. of phosphate.

b. To employing nitro-hydrochloric acid as a solvent for the

*Zeitschr. f. angew. Chem. 1891, 8, p. 243.

†Ibidem, 1891, p. 170.

‡Zeitschr. f. anal. Chem., 30, pp. 206, 207.

§H. H. B. Shepherd, Chem. News, May 29, 1891, p. 251.

raw phosphate and consequently including in the oxides of iron and aluminum any iron present in the form of pyrites.

c. To the plan of dividing the phosphate of iron and aluminum found by two, to obtain the oxides instead of determining the phosphoric acid in the precipitate, and deducting this from the total.

Modified method :

2.5 gms. of the phosphate are dissolved in 10 cc. of hydrochloric acid and evaporated to dryness, taken up with hydrochloric acid, raised to the boiling point, washed into a 250 cc. flask with as little water as possible, 10 cc. of strong sulphuric acid added, and the solution allowed to stand for about 5 minutes with frequent shaking.

Some 95 per cent. alcohol is now added, the mixture cooled, made up to the mark with alcohol and well shaken. Owing to the contraction in volume which takes place, it must again be made up to the mark and mixed. It is now allowed to stand for one hour, filtered, 200 cc. of the filtrate taken and gently evaporated to a small bulk in a dish. It is desirable when organic matter is present to carry the evaporation to pastiness, so that the acid may effect its partial destruction. It is then washed into a beaker with about 50 to 100 cc. of water, boiled for a short time with a few drops of bromine or some other oxidizing agent, ammonia added in excess, again boiled for half an hour, cooled, a little more ammonia added to make sure that a slight excess is present, filtered, washed with a hot solution of ammonium chloride, ignited and weighed. Unless ammonium chloride is present, the precipitate is very apt to wash through even a very close filter. When the weight of the phosphates has been obtained, the precipitate is redissolved, and the phosphoric acid in it determined, the amount so found, deducted from the total weight, giving the oxides by difference. Of course if the oxide of iron is required apart from the alumina, a separate iron determination must be made.

The following postscript was suggested by Messrs. Teschemacher and Smith.

Should the phosphate under examination contain any magnesia, the phosphates of iron and alumina obtained in the foregoing process must be freed from this impurity by washing the precipitate

from the filter and boiling with water and a little nitrate of ammonia, repeating this treatment, if after first application, the filtrate still shows any magnesia.

Dr. J. H. Vogel* reports series of experiments made by him on the estimation of calcium by Jones' method and on the presence of magnesia in the precipitate.

With regard to the former he concludes that the calcium is precipitated quantitatively as sulphate and as to the latter he makes the following statement :

1. That when only small amounts of magnesia are present it all passes quantitatively into the ammoniacal filtrate.

2. That with Glaser's method, as much as 3 to 3.5 per cent. magnesia, and with Jones' modified method as much as 1.5 per cent. may be present, there being no danger of its being precipitated with the iron and aluminum as long as care is taken to remove all the free ammonia by boiling.

3. That after the magnesia has come down with the phosphates, it will not redissolve on boiling, magnesium-ammonium phosphate being only sparingly soluble in hot water.

The same author has also proposed to combine the Glaser and Stutzer methods (the latter as modified by himself). If the lime is to be estimated, he advises the use of Jones' method. The alcohol is expelled from the filtrate from the calcium sulphate, the phosphates of iron and aluminum precipitated and then analyzed by the modified Stutzer method. In the filtrate from the phosphates the magnesia may be thrown down by adding an excess of ammonia and allowing it to stand over night.

As I stated before, the conventional method is an unreliable one, and undoubtedly the alcohol method is a great improvement, as it has never failed to give concordant, and therefore, comparative results as applied to ordinary phosphate rocks in the hands of different chemists. Thus, where simply an approximation of the amount of iron and alumina is desired, it is of great value, the errors involved remaining very nearly constant. But when accurate work is desired, it has, as proposed, few advantages over the old method, one of the strongest objections being that of the Chemical Manure Manufacturers' Association with regard to di-

*Zeitschr. f. angew. Chem. 1891, 12, p. 357.

viding the total weights of phosphates by two, calling one-half the sum of the ferric and aluminic oxides. To eliminate the error thus introduced, we must make a phosphoric acid determination in the precipitate, and the method becomes long and tedious.

Considering the ease and rapidity with which accurate results are obtained by the molybdate method as I used it, I would prefer the latter at all times. During my work I tried the Glaser method, its modification by Jones, the combined Jones-Stutzer method as proposed by Vogel, and the molybdate method as used by Mr. McElroy.

EXPERIMENTS ON THE GLASER METHOD.

In the first estimations made by this method, I noticed, when the alcohol was evaporated, the formation of crystals of calcium sulphate, and therefore discarded it, as these crystals would contaminate the phosphate-precipitate.

EXPERIMENTS ON JONES' METHOD.

This method separated the calcium perfectly. In boiling off the alcohol, I noticed the formation of aldehyde, which was accompanied by a reduction of the iron. It is therefore necessary before adding the ammonia, to boil for a few moments with a few drops of nitric acid. Jones claims that the calcium is separated quantitatively, and that the alcohol is diluted sufficiently by the water present to keep the bases in solution. While working with this method I noticed that the ignited calcium sulphate was invariably slightly rose colored. Upon investigation, I found this to be due to small quantities of iron, which were precipitated by the alcohol. I then tried to remove this by continued washing of the freshly precipitated calcium sulphate, but even after using a liter of 85 per cent. alcohol I still found the calcium sulphate contaminated with iron. Here then there is a grave source of error which is no doubt due to the large quantity of alcohol used, as I never observed any iron in the calcium sulphate obtained by Glasers' method. Through lack of time I did not determine the quantities of iron thus taken down, but they were considerable, and increased with the percentage present in the original substance.

I was here curious to investigate the action of potassium and

ammonium salts on the precipitation of the calcium, and my work led me to some astonishing results.

Four solutions were made, as follows :

1. An unknown solution of calcium phosphate, the latter being brought into solution by means of a little hydrochloric acid.
2. A solution of potassium chloride containing 1.0 gm. in 100 cc.
3. A solution of ferric chloride containing .022 gm. Fe_2O_3 in 10 cc.
4. A solution of ammonium chloride containing 1.0 gm. in 100 cc.

The calcium was precipitated according to Jones. It was first estimated in the calcium phosphate solution, 25 cc. being used with 10 cc. of the ferric chloride solution.

Two estimations gave calcium sulphate :

.2519 gm.

.2519 "

These agree exactly, but both were slightly rose-colored. A mixture was then made of 25 cc. of calcium solution, 10 cc. of the iron solution, and 5 cc. of the potassium chloride solution. Two estimations gave calcium sulphate :

.2785 gm.

.2784 "

Both of these were highly colored with iron, and a qualitative examination revealed the presence of potassium.

Then 25 cc. of the calcium solution, 10 cc. of the iron solution, and 10 cc. of the potassium chloride solution were mixed, and the calcium separated and weighed.

Two estimations gave calcium sulphate :

.2805 gm.

.2800 "

These two contained still more iron, and potassium was again present.

The influence of the ammonium chloride was then tried. I again used 25 cc. of the calcium solution, 10 cc. of the iron solution, and 5 cc. of the ammonium chloride solution.

Two estimations gave calcium sulphate :

.2541 gm.

.2543 "

and on using the same mixture with 10 cc. of the ammonium chloride solution, I obtained calcium sulphate :

.2563 gm.

It thus appears that the presence of potash and ammonium salts increases the amount of iron present in the calcium sulphate. The presence of the alkali shows that the alcohol precipitates it and the iron, as double sulphates or alums which are much less soluble in alcohol than any other ferric and aluminic salts.

Ammonium salts do not exercise this influence to so great an extent as potassium salts, but still sufficiently to vitiate the subsequent results. This renders the Jones method inapplicable in cases where these alkalies are present, as in soils and ashes and the presence of small quantities of iron, even in those instances where no alkali was added, indicates that the quantity of alcohol prescribed by Jones is too high.

It is of interest to note the manner in which the presence of potassium or ammonium salts influenced the form in which calcium sulphate precipitated. Usually when the alcohol is added the precipitate in a very short time becomes crystalline. When these salts, however, are present, it precipitates in a flocculent form, and remains so, even if allowed to stand over night.

Finding in this manner possibilities of error which rendered both methods doubtful, I decided to try the Stutzer method as modified by Vogel, with previous removal of the calcium, according to Glaser's directions. In two other portions of the solution the calcium was precipitated according to Jones.

I append the results obtained with a phosphate rock :

Sample.	Method.	Weight Material.	Weight Precipitate.	Per cent. Combined Oxide.
I.	Glaser-Stutzer	.500 gm.	.0085	1.70
I.	"	.500 "	.0084	1.68
I.	Jones-Stutzer	.500 "	.0028	.56
I.	"	.500 "	.0032	.64

We see that much less iron and aluminum was present in the alcoholic filtrate obtained by Jones' method and this is another proof that some of it is retained by the calcium sulphate.

I now turned to the molybdate method used by Mr. McElroy,

it appearing that this should, if properly and carefully carried out, give accurate results. On a preceding page, I have given a description of this method. It is necessary to resort to a double precipitation of the hydrates, as when the ammonia is first added a small amount of molybdic anhydride is liable to separate out in the form of a white powder. If the liquid is kept as cool as possible, and the ammonia added only in slight excess, this is reduced to a minimum. It never occurs in the second precipitation.

The method was tried on four phosphate rocks and gave the following results:

Sample.	Weight Material.	Weight Precipitates.	Per cent. Oxides.
1200 gm.	.0052	2.60
1200 "	.0053	2.65
2200 "	.0022	1.10
2200 "	.0021	1.05
3200 "	.0064	3.20
3200 "	.0068	3.40
4200 "	.0099	4.95
4200 "	.0100	5.00

Sample 1 is the same as that to which the Stutzer method was applied, and we see that the molybdate method gives much higher results, which from the nature of the method are undoubtedly much more accurate.

This method was tried with success in the analysis of soils by Mr. J. L. Fuelling. By permission, I include some of his results.

Sample.	Per cent. Oxides.	Sample	Per cent. Oxides.
<i>a</i>	2.32	<i>c</i>	1.19
<i>a</i>	2.26	<i>c</i>	1.19
<i>b</i>	1.48	<i>d</i>	1.23
<i>b</i>	1.55	<i>d</i>	1.23

The greatest deviation between duplicates, we see, is .07 per cent., an allowable difference which occurs in all analytical work.

All in all, the above shows that this method is to be preferred to all others, being as short and as rapid as the alcohol method, giving more accurate and concordant results, and giving the oxides in a form which is easily rendered soluble, so that the iron can be accurately estimated.

XVIII. EXAMINATION OF A BUTTER ADULTERANT.*

By H. W. WILEY.

A few days ago, Mr. H. J. Fish, Superintendent of the Producers' Dairy Co., 324 B St., S. W., Washington, D. C., brought to me a sample of genuine butter, together with a sample of artificial butter prepared by taking equal parts, by weight, of the genuine butter and milk, and churning them together with the addition of a small quantity of the substance known as "Gilt Edge Butter Compound" from the Planet Manufacturing Company, of Wichita, Kansas. The directions for the use of it are to take a pint of fresh unskimmed milk and as much of the compound as you can heap on a silver ten-cent piece, and thoroughly mix the compound and milk together in the churn with as much salt as is necessary to salt one pound of butter. Add to this one pound of soft butter and churn until the whole mass has come to butter, when you will have two pounds of butter and no milk. It is directed that the genuine butter should not be melted, but made very soft and pliable, so that the churn dasher will easily go through it. The milk should be warmed to the temperature at which it is taken from the cow. The churn should always be scalded or warmed sufficiently to prevent chilling the milk, plenty of salt added, and butter color, if used, before churning. It is particularly enjoined that the butter should not be worked, but should be made into rolls and put into jars and set away in a cool place to harden.

The sample of genuine dairy butter, which was furnished with the compound, was found to contain :

Water	15.92 per cent.
Butter-fat	80.53 "
Ash	0.38 "
Curd and undetermined	3.17 "

This represents a fair sample of butter, with the exception that the water is a little higher than the average. In the premium butters obtained at the Chicago Dairy Show, in 1889, the percentage of moisture varied in ten samples from 8.69 per cent. to 11.86 per cent.

The artificial butter prepared from the above by the Producers'

*Read before the Washington Chemical Society, Nov. 12, 1891.

Dairy Company was subjected to analysis, and the following numbers were obtained :

Water	49.55 per cent.
Butter-fat	45.45 "
Ash	1.34 "
Curd and undetermined	3.66 "

There was no doubt at all that the Gilt Edge Butter Compound would do what was claimed for it, inasmuch as Mr. Fish had made the butter himself according to the directions.

We also submitted the compound to a practical test in our laboratory and found that with one pound of butter, one pint of milk and about one gram of the butter compound, we could easily make two pounds of material which resembled very closely a first-class article of butter, except that it was considerably softer.

I at once suspected that the compound contained some emulsifying substance, either of a mineral nature or some organic ferment. On subjecting the butter compound to analysis, it was found to contain 70.48 per cent. of anhydrous sodium sulphate, and 29.52 per cent. of organic matter. This organic matter responded perfectly to the test for pepsin, and it is undoubtedly pepsin. Whether a pure pepsin or a crude form, was not determined. Having established the fact that this is pepsin, experiments were made with pepsin and other digestive ferments, viz., pancreatin and trypsin. These bodies act as pepsin and produce an emulsion, which enables butter to incorporate an equal weight of milk in its substance, without materially altering its appearance. The experiments were also tried with rennet and it was found to act in the same way ; whence we may conclude that all the digestive ferments when beaten up with milk and butter in the manner indicated will produce an emulsion apparently causing the milk to entirely disappear.

The Gilt Edge Butter Compound is colored pink with some organic coloring matter in order to obscure its real nature. The anhydrous sodium sulphate seems to be added simply as a carrying material and it is not supposed to produce any active effect in the emulsifying process. In fact, pepsin pancreatin, trypsin and rennet used without anhydrous sodium sulphate produce exactly the same emulsifying effect as the Gilt Edge Butter Compound.

By this simple device, the unprincipled dealer could easily impose upon his customers, furnishing them with an article of butter containing only half the portion of that substance without greatly diminishing its price. The keeping properties, of course, of the emulsified butter would not be so great, but for rapid home consumption this would not be noticed.

The analysis of the butter and butter substitutes and of the "Gilt Edge Compound" and the preparation of the samples of adulterated butter made with rennet, pepsin, pancreatin and pepsin were conducted by Mr. W. H. Krug.

[CONTRIBUTIONS FROM CHEMICAL DIVISION U. S. DEPARTMENT
OF AGRICULTURE.]

XIX. COMPOSITION OF ARTIFICIAL CRYSTALS OF CALCIUM PHOSPHATE.*

BY H. W. WILEY AND W. H. KRUG.

The basic slag, resulting from the manufacture of steel, by the basic process, under the patents of Mr. Jacob Reese, has only lately come into use in this country for fertilizing purposes. Vast deposits of natural calcium phosphate have, up to within a year or two, prevented the profitable marketing of the basic slag. Perhaps a more accurate statement would be that the failure of our agriculturists to appreciate the value of basic slag as a fertilizer has had a more potent influence in this respect than the competition of natural phosphates. Mr. Reese, after many years of litigation, has finally been awarded priority for his claims as the inventor of the basic process. It is therefore more appropriate, from a legal point of view, at least in this country, to call the slag by his name than by the name of Thomas, as is done in Europe. The large steel furnaces at Pottstown, Pa., have placed upon the market a fine article of slag phosphate, which, from the name of the inventor, is called "Reese's odorless phosphate."

A few months ago Mr. Reese sent me a sample of the crystals of calcium phosphate taken from the Pottstown furnaces, accompanied by the following statement:

"As a matter of interest to you, I will send you this day by express, a sample of crystallized tetrabasic phosphate. It is one of

*Read before Washington Chemical Society, Nov. 12, 1891.

the finest specimens I have ever seen. The pure crystals have the following composition :"

Ca	42.901 per cent.
P	16.606 "
Mg	0.494 "
Fe	0.072 "
V	0.646 "
O	39.181 "
Loss and undetermined	0.100 "

Mr. Reese gave the following as the composition of the crystals :

(CaO) ₄ P ₂ O ₅	98.250 per cent.
MgO	0.828 "
Fe ₂ O ₃	0.100 "
VO	0.722 "
Undetermined	0.100 "

A part of the sample sent by Mr. Reese, showing the crystals of calcium phosphate, is shown as a specimen. Two kinds of crystals were distinguished ; first a tabular form, generally transparent, of a light yellow color varying to dark brown, and second an acicular form dark green by reflected light and bluish green by transmitted light.

Considerable quantities of these two classes of crystals were carefully separated and subjected to analysis. The acicular crystals only were found to contain vanadium. The analysis gave the following results :

	Acicular Crystals.	Tabular Crystals.
Calcium oxide	42.69	53.61
Ferric oxide	20.98	9.64
Aluminic oxide	3.71	0.91
Magnesia	0.49	0.08
Vanadium dioxide	0.18	. .
Phosphoric anhydride	27.06	33.92
Silica	4.96	1.75
Total	100.07	99.91

Different methods of combining the material or substances found in the crystals may be suggested. Regarding the crystals as tetrabasic calcium phosphate, the following combinations are admissible :

Acicular Crystals.

$\text{Ca}_4\text{P}_2\text{O}_9$	62.20 per cent.
Fe_2O_3	18.36 "
CaSiO_3	9.59 "
Fe_3PO_4	4.95 "
Al_2O_3	3.71 "
$\text{Mg}_4\text{P}_2\text{O}_9$	1.08 "
V_2O_5	0.18 "
Sum	100.07 "

or in the second place—

$\text{Ca}_4\text{P}_2\text{O}_9$	69.70 per cent.
Fe_2O_3	20.98 "
SiO_2	4.96 "
Al_2O_3	3.71 "
MgO	0.49 "
V_2O_5	0.18 "
Sum	100.02 "

In the tabular crystals the following probable combination may be assumed :

$\text{Ca}_4\text{P}_2\text{O}_9$	84.93 per cent.
Fe_2O_3	8.55 "
CaSiO_3	3.38 "
Fe_3PO_4	2.06 "
Al_2O_3	0.91 "
MgO	0.08 "
Sum	99.91 "

or, $\text{Ca}_4\text{P}_2\text{O}_9$	87.43 per cent.
Fe_2O_3	9.64 "
SiO_2	1.75 "
Al_2O_3	0.91 "
MgO	0.08 "
Sum	99.81 "

There is little doubt of the fact that the second form of combination in the two cases given above is the proper one, unless the silica exist combined with lime as indicated in the first form. In other words, the lime and phosphoric acid present in the crystals are combined in the form of tetrabasic calcium phosphate. In the acicular crystals this method of calculation gives an excess of

.05 per cent. phosphoric acid and in the tabular crystals of .10 per cent. of lime, but these excesses can easily be ascribed to analytical errors, thus leaving the whole of the lime and phosphoric acid united as mentioned.

The striking differences between these analyses and those furnished by Mr. Reese are shown in the presence of iron, silica and alumina. In the crystals submitted to analysis by him were found scarcely any constituents except the tetrabasic phosphate. In those submitted to examination in our laboratory considerable quantities of impurities, chiefly iron and alumina, were discovered. Owing, however, to the definite crystalline form, it appears that these impurities were not in sufficient quantities to disturb the crystalline forces. The presence of vanadium in the acicular crystals is interesting, although the amount discovered in our laboratory was much inferior to that in the analysis by Mr. Reese.

It might be interesting also to account, or at least try to account for the presence of tri-calcium phosphate only in the samples under analysis. Computing the lime as tri-calcium phosphate, it is found that in each case there is considerable of an excess of this element. In the case of the acicular crystals, the composition would probably be something like the following :

$\text{Ca}_3\text{P}_2\text{O}_8$	59.07 per cent.
Fe_2O_3	20.98 "
CaSiO_3	9.58 "
CaO	6.06 "
Al_2O_3	3.71 "
MgO	0.49 "
V_2O_5	0.18 "
Sum	100.07 "

In the tabular crystals, the probable composition, on the above assumption, would be as follows :

$\text{Ca}_3\text{P}_2\text{O}_8$	84.05 per cent.
CaO	1.85 "
Fe_2O_3	9.64 "
CaSiO_3	3.38 "
Al_2O_3	0.91 "
MgO	0.08 "
Sum	99.91 "

There is little use of discussing here the above assumption, as there is no doubt whatever of the fact that the lime and phosphoric acid are combined chiefly as tetracalcium phosphate.

The study of the crystals of tetrabasic calcium phosphate is not new in chemical literature. As long as four years ago Hilgenstock prepared artificial crystals of this salt and published a description of them.* This artificial salt was prepared by fusing tricalcium phosphate, di-calcium phosphate and phosphoric acid with a calculated amount of lime. Calcium fluoride was used as a flux. Iron and vanadium being excluded from this mixture, the crystals obtained were colorless needles, which gave on analysis 38.51 per cent. of P_2O_5 , and 60.08 per cent. of lime and a trace of silica. Hilgenstock noticed at this time that the corresponding acicular crystals appearing in the slag from the furnaces are colored brown or black by a mixture of metallic oxides. He, however, did not notice the presence of vanadium as one of them. Hilgenstock explains the different crystalline forms as being due simply to the temperature at which crystallization takes place. He states, moreover, that the tetrabasic phosphate is invariably the form in which phosphoric acid occurs in Thomas slag. Tribasic phosphate is reduced by metallic iron at the melting point, but metallic iron does not have this effect upon the tetrabasic salt.

Observations on the grouping of the crystals in the slag blocks tend to show that the first crystals to appear are the tabular ones. After these come the brown hexagonal needles, and towards the last when the fluid heart of the block begins to solidify and become richer in silica, the deeply colored lustrous forms of crystals appear. Hilgenstock obtained by melting the rhombic tables with calcium fluoride, hexagonal crystals. He also states that silica invariably appears as calcium silicate, which, however, would not be the case with the samples examined in our laboratory, on the assumption that the whole of the phosphoric acid was combined with calcium. If we assume that a sufficient amount of calcium is obtained for the formation of calcium silicate, then the excess of phosphoric acid in that case would go to the iron or the alumina.

Rücking and Linde† also make a number of observations on the crystalline forms in which tetracalcium phosphate appears in slag.

*Stahl und Eisen, 7, p. 557.

†Stahl und Eisen, 4, p. 245.

After the treatment of the sample with a magnet, three different compositions of crystals in the slag were separated by differences in specific gravity. The method of separation is not stated, but was probably by Thoulet's solution consisting of a mixture of iodide of mercury and potassium in varying proportions. The analytical data obtained on the three samples of material of different specific gravities were as follows :

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
P ₂ O ₅	36.77	31.19	38.77
SiO ₂	3.81	9.47	0.89
Cl	trace
S	trace	0.28
Al ₂ O ₃	1.09	1.13	} 0.89
Fe ₂ O ₃	1.78	. .	
FeO	2.22	0.95	. .
Mn	trace	trace
CaO	53.51	57.42	59.53
MgO	0.40	trace	trace

Sample No. 1 dissolved in hydrochloric acid separated gelatinous silica. Part of the phosphoric acid, however, was replaced by parasilicic acid, and part of the calcium by iron, magnesia and alumina.

In product No. 2 were found crystallized together particles of forms Nos. 1 and 3 hard to separate. In this form also it is probable that a part of the phosphoric acid in combination with the lime is replaced by silica.

The form No. 3 is found in tabular crystals varying from clear to deep brown. It may be regarded, according to the authors, as a salt of the undiscovered acid H₄P₂O₇. A small portion of the phosphoric acid is also replaced by the silica in this compound.

It may be of interest in this connection to give a few comparative data of the composition of basic slag analyses in Europe, although no attempt is made to give a complete list of the analyses which have been printed.

Jensch* gives the following composition of basic slag before and after boiling with a sugar solution. The object of boiling with the sugar solution was to extract any uncombined calcium oxide which the slag might contain.

*Chem. Industrie, 1887, 12; Bied. Centralblatt f. Agr. Chem., (1888), 17, 12.

Commercial Thomas Slag Meal.

	Natural Meal.	After Boiling with Sugar Solution to Extract Lime.
	Per cent.	Per cent.
SiO ₂	5.23	6.22
P ₂ O ₅	20.15	23.99
CaO	54.06	45.73
MgO	4.39	5.23
FeO	7.09	8.44
Fe ₂ O ₃	4.87	5.79
MnO	1.21	1.44
Al ₂ O ₃	1.35	1.61
S	0.24	0.28
SO ₃	0.57	0.60
CO ₂	0.74	0.91

Otto* gives the following as the result of the analysis of a sample of basic slag and the probable form of combination of the constituents.

<i>Found.</i>		<i>Calculated.</i>	
	Per cent.		Per cent.
P ₂ O ₅	19.03	Ca ₄ P ₂ O ₉	49.02
SiO ₂	8.20	CaSiO ₃	15.85
MnO	5.24	CaO free	11.00
FeO	8.06	CaS	1.35
Fe ₂ O ₃	5.14	MnO	5.24
CaO	49.90	FeO	8.06
S	0.60	Fe ₂ O ₃	5.14
MgO	3.40	MgO	3.40
Al ₂ O ₃	1.10	Al ₂ O ₃	1.10
CO ₂	trace		

The crystals found in this sample of slag gave upon analysis the following numbers :

P ₂ O ₅	38.75 per cent.
CaO	61.30 "

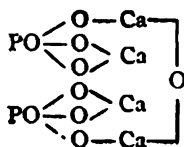
While the theoretical composition of pure tetracalcium phosphate is :

P ₂ O ₅	38.80 per cent.
CaO	61.27 "

These crystals therefore are almost absolutely pure tetracalcium

*Chemiker Ztg. 1887, No. 18, 255.

phosphate. The probable form of combination of the atoms in the molecule of tetracalcium phosphate is given by Kormann as follows:



It would be interesting to push this investigation further and see under what conditions the crystals obtained are pure tetracalcium phosphate and under what conditions they contain a large amount of metallic oxides as found in those examined by us. A mere inspection of the crystals would usually be sufficient to determine whether or not there is a metallic admixture of those oxides, as a deep color would at once indicate considerable quantities thereof. Inasmuch as the estimation of vanadium is one which we are rarely called upon to perform, it may be of interest to append a few of the present methods which are practiced for this purpose. The one used by us is the last one, viz., Lindemann's, which is a volumetric method and appears to be accurate as well as speedy.

METHODS OF ESTIMATING VANADIUM.

Blair* gives the following method:

Treat 5 gms. of the drillings with 50 cc. of nitric acid (sp. gr. 1.20) in a No. 4 beaker. When all action has ceased, transfer the liquid to a porcelain dish, evaporate to dryness and heat at a gradually increasing temperature over a Bunsen burner until the nitrates are nearly all decomposed and the mass separates easily from the bottom and sides of the dish. Transfer the cool mass to a porcelain or agate mortar, and grind it thoroughly with 30 gms. of dry sodium carbonate and 3 gms. of sodium nitrate.

Transfer to a large platinum crucible and fuse well for about an hour at a high temperature. Run the fused mass well up the sides of the crucible, allow it to cool, dissolve in hot water and filter. Dilute the filtrate to about 600 cc. and add nitric acid carefully to get rid of the carbonic acid. Boil off the latter, but

*The Chemical Analysis of Iron, p. 103.

be careful to keep the solution always slightly alkaline. Add nitric acid, drop by drop, until the solution is just acid, then add a few drops of carbonate of sodium solution to render solution faintly, but decidedly alkaline. Boil for a few minutes and filter. To the filtrate add a few drops of nitric acid to make it faintly acid when the appearance of the yellowish coloration is an indication of the presence of vanadic acid. Add to the solution a few cc. of mercurous nitrate and then an excess of mercuric oxide in water to render the solution neutral and insure the complete precipitation of all the mercurous vanadate. With the mercurous vanadate are precipitated also all the phosphoric, chromic, tungstic and molybdic acids as mercurous salts. Heat to boiling, filter, and wash the precipitate. Dry, separate the paper, burn it in a platinum crucible, add the precipitate, heat carefully to expel the mercury, and finally heat to full redness. Fuse the brownish red mass remaining in the crucible with a small amount of sodium carbonate and a pinch of sodium nitrate. Dissolve the cooled mass in a small amount of water, and filter into a small beaker. Add to the solution pure ammonium chloride in excess (about 3 to 5 gms. to each 10 cc. of solution), and allow it to stand for a time, stirring occasionally. Vanadate of ammonium, insoluble in a saturated solution of ammonium chloride, separates out as a white powder. It is necessary to keep the solution decidedly alkaline, and a drop or two of ammonia must be added from time to time. The appearance of the faintest yellowish tint to the solution is evidence that the solution has become slightly acid, and this must be corrected, or the result will be too low. Filter on a small ashless filter, wash first with a saturated solution of ammonium chloride containing a drop or two of ammonia, and then with alcohol. Dry, ignite, moisten with a drop or two of nitric acid, ignite, and weigh as V_2O_5 , which contains 56.22 per cent. vanadium.

QUANTITATIVE ESTIMATION OF VANADIUM AND SEPARATION
OF VANADIC ACID FROM PHOSPHORIC ACID.*

The author finds that by the application of Rosenheim's iodometric method (*Annalen*, 251, 197) vanadic acid may be rapidly and exactly determined after first precipitating it as barium or

*R. Holversheet, Chem. Centr. (1890), 1, 977; J. Chem. Soc., Nov., 1890, p. 1343.

lead vanadate. The substance is dissolved, and the vanadic acid precipitated with barium chloride or lead acetate. The precipitate is boiled with HCl and potassium bromide, and the liberated bromine determined volumetrically with potassium iodide. In the absence of substances like molybdic acid, which are reduced by sulphurous acid or hydrogen sulphide, the vanadic acid may also be determined by reducing it, boiling off the excess of reducing agent, and determining the VO_4 by permanganate.

If the vanadic acid has been separated as barium or lead vanadate, the metal must first be separated before liberating with permanganate.

For the determination of phosphoric acid and vanadic acid when they occur together, the vanadic acid is first reduced to the tetroxide. The excess of reducing agent is expelled, and the phosphoric acid then precipitated with molybdic acid and filtered off. If the amount of vanadic acid is large, the precipitation of phosphomolybdate should be done rapidly at 55° to 60° C., using a considerable excess of molybdic acid; or the vanadic acid may first be determined in the solution by boiling with hydrochloric acid and potassium bromide, estimating the liberated bromine as usual.

The phosphoric acid is determined by evaporating the solution with a little sulphuric acid to dryness, taking up the residue with water, reducing the vanadic acid with sulphurous acid, and precipitating the phosphoric acid by means of molybdic acid.

If alkalies are to be determined, the substance is dissolved in acetic acid, is treated at the boiling point with lead acetate, the lead vanadate filtered off, and the alkalies estimated in the filtrate.

Lindemann* gives the following method:

Dissolve 4 gms. of the finely powdered slag in 60 cc. of dilute sulphuric acid [1 volume H_2SO_4 , sp. gr. 1.84, to 4 volumes of water], boil a few moments, cool, make up to, say 80 cc., filter, and take 40 cc. for analysis. Add potassium permanganate solution (about decinormal) till there is a slight pink color to ensure oxidation of the vanadium to V_2O_5 . Add, drop by drop, a weak solution of ferrous sulphate till the pink color just disappears. The vanadium is then present as a sulphuric acid solution of V_2O_5 . Run in freshly prepared ferrous sulphate of known strength (2.183

*Ztschr. f. anal. Chem. 18, (1879), p. 99.

gms. pure iron dissolved in sulphuric acid and made up to one liter), till a drop of liquid taken out of the beaker just begins to show a greenish-blue tinge when it touches a drop of ferricyanide of potash.

Note the ferrous sulphate used :

1 cc. = .002 gm. V.
.002888 gm. V_2O_5 .
.003648 gm. V_2O_5 .

In practice Ridsdale modifies the method as follows :

First add a little water to the powdered slag, boil, then add the dilute sulphuric acid.

Determine the value of the ferrous sulphate solution with $\frac{n}{10}$ potassium dichromate solution.

We desire to express our obligations to Mr. K. P. McElroy for his assistance in the preparation of this paper.

ANIMAL, MARINE AND VEGETABLE OILS USED IN LUBRICATION. THEIR CHEMICAL REACTIONS, AND THE METHODS OF DETECTION IN MIXTURES.

BY PROF. THOMAS B. STILLMAN.

[Continued from page 324.]

Gibb's viscosimeter, Fig. 13 (George Gibbs, M.E., Chicago, Milwaukee and St. Paul Railroad), was designed to overcome some objectionable points in existing forms of viscosimeters.

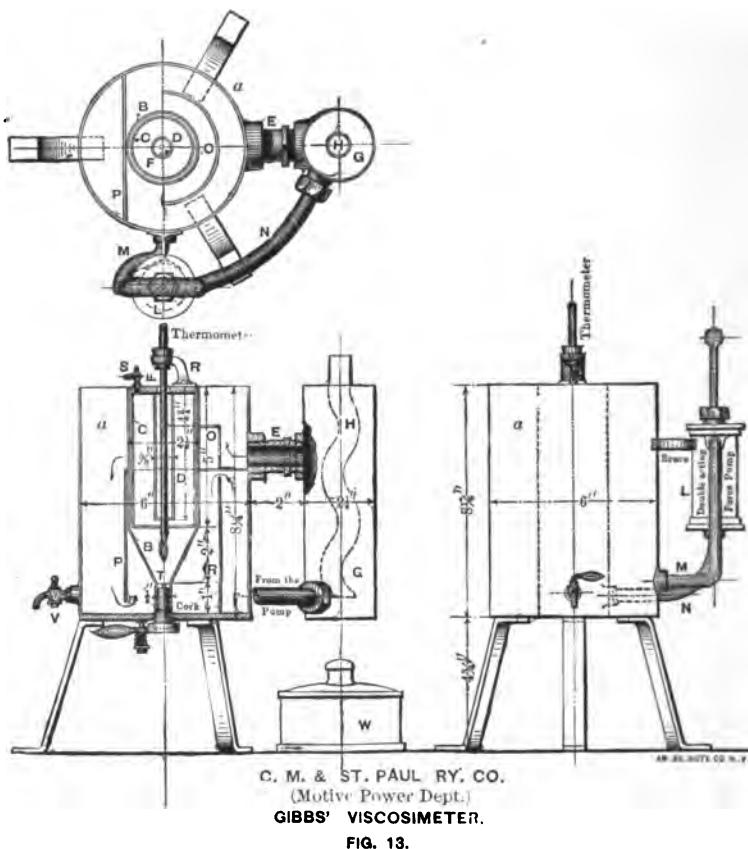
The idea being: *First*.—To have a large body of hot oil as a bath surrounding the oil to be tested in order to keep the latter at a perfectly uniform temperature.

Second.—To apply a forced circulation to the bath by means of a double action pump, to insure equality of heat in all parts.

Third.—To deliver the oil to be tested at the orifice under a constant head, which is accomplished by means of a pneumatic trough.

Fourth.—To supply convenient means for accurately measuring the temperature of the oil near its delivery point.

The large reservoir *a* is of copper, with heavy brazed bottom. This contains the cylindrical inside chamber with conical bottom *B*. At the lower end of this is the gauged aperture *T*. Inside of this chamber fits the inverted reservoir *C*, holding the oil to be tested. In the interior of this chamber is a tube *D* extending



nearly to the bottom of the same. This tube admits air to determine the head of the oil, and also to admit the thermometer *F*. The outside bath *a* contains the deflector plates *O*, *P* and *R* to obtain proper mixing of the bath. The heating of the bath is done by a lamp *W*, set underneath the separate heating chamber *G*. The size of the orifice at *T* is $\frac{1}{16}$ inch.

The following table shows the results of viscosity tests upon various oils made with this instrument.

Viscosities of Valve Oils and Stocks.

	Gravity. Baume.	Flash.	Per cent. Mineral Oil.	VISCOSITIES.			
				250° F.	300° F.	350° F.	400° F.
Nat. Ref'g Co., Loco. Cyl. .	26.8°	F. 525°	75.7	38 sec.	32	26	..
Nat. Ref'g Co., German . .	25.8	550	70.0	43	33	28	..
Perfection valve oil	26.0	510	54.7	35	29	25	..
" " "(another)	25.7	undet.	63.0	34	28	24	..
" " "	25.9	510	undet.	23	21
Vacuum valve oil	25.2	535	95.0	27	23
C., M. & St. Paul valve oil .	26.4	485	66.7	23	21
Ex. lard oil (av. of 3 samples)	25	23	21	20
Standard Oil Co., No. 1 stock	27.0	520	100	46	32	26	22
" " " 2 "	27.3	510	100	47	32	26	22
" " " 3 "	27.8	490	100	39	30	25	21
" " " 4 "	26.2	525	100	46	33	27	23

Viscosities expressed in seconds for 50 cc.

Viscosities of Car and Engine Oils.

	Gravity. Baume.	Flash.	Per cent. Mineral Oil.	VISCOSITIES.		
				75° F.	110° F.	150° F.
National Ref'g Co., car oil	30.8°	F. 200°	100	223	68	41
Relief Oil Works, "	30.4	200	100	163	61	38
Galena car oil	28.5	160	90	102	54	36
" " "	28.2	165	90	83	50	33
" " "	28.7	155	90	102	54	36
" " "	27.8	170	90	88	52	34
" " "	26.3	285	91.9	234	99	49
" " "	26.5	260	91.0	257	98	48
Relief Oil Works, engine oil	30.1	210	100	130	64	37
National Ref'g Co., " "	26.5	385	100	740	113	54

Viscosities expressed in seconds for 50 cc.

The viscosities of a number of other oils, at the temperature of locomotive cylinders, as made by this instrument, are shown in the following chart of curves (Fig. 14).

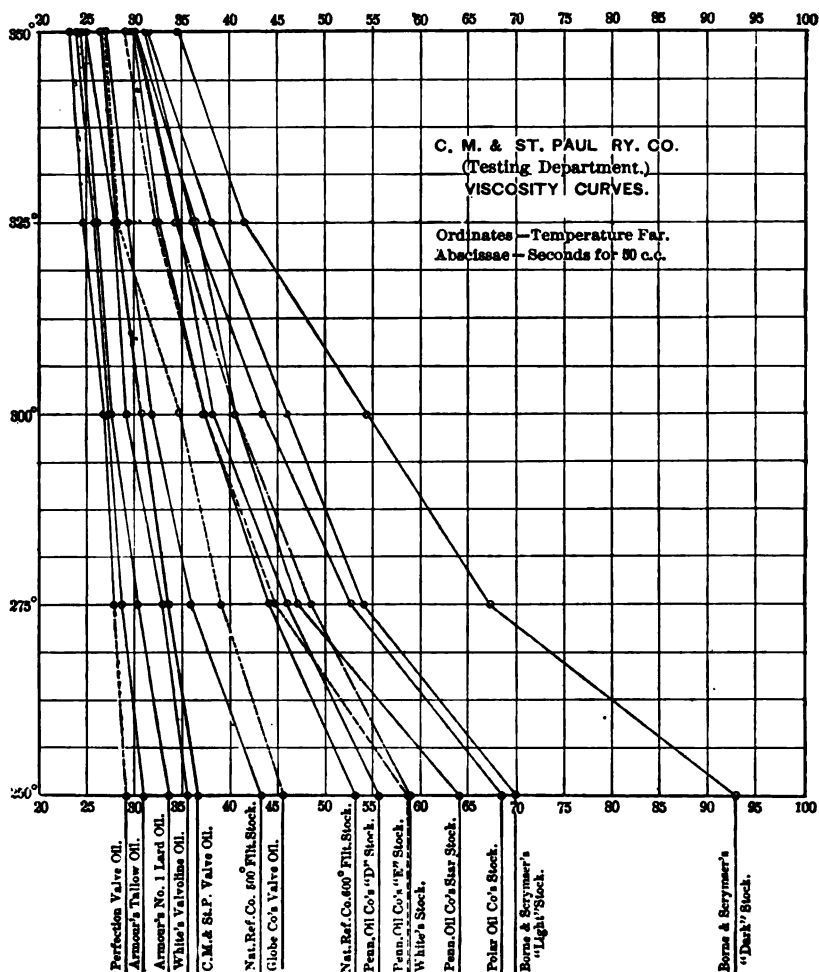


FIG. 14.

A viscosimeter on an entirely different principle than the others already described is the Perkins instrument (G. H. Perkins, Supt. Atlantic Oil Refinery, Phila., Pa.). It consists of a cylindrical vessel of glass, surrounded by a proper heating vessel, and fitted with a piston.

This piston fits into the cylinder to within $\frac{1}{1000}$ of an inch.

In practice, the cylinder is filled nearly full with the oil to be

tested and the piston inserted. The time required for the piston to sink a certain distance into the oil is taken as the measure of viscosity. A full description of the apparatus will be found in *Transactions of the American Society of Mechanical Engineers*, 9, 375.

J. Lew (*Ding. Poly. Jour.* 1801, p. 280) introduces an instrument not only for the viscosity, but also to include the internal friction of an oil. By these means it is claimed the lubricating value of the oil is absolutely determined.

The author states that the internal and external frictional resistances are different, and vary in the different oils at various temperatures. Formulæ and methods are given by which coefficients are determined and used in the examination of the lubricating value of oils.

Fig. 15 represents the viscosimeter designed and used in my laboratory at the Stevens Institute of Technology.

It consists of a copper bath *B* surrounding the vessel *A*, also of copper, and which holds the oil whose viscosity is to be determined. The tube *f* is of copper, but at *e* it is joined to a glass tube, which is extended to *d*—this latter is used for measuring the oil, and is carefully graduated. Sizes and dimensions of the apparatus are given in the figure.

This apparatus was designed to overcome two difficulties usually occurring in the use of other viscosimeters, viz.: *First*, loss of heat in the oil during its passage from the containing vessel to the receiving flask; and *second*, to have the chamber *A* of size to work small quantities of oil. *First*.—When the viscosity of an oil is taken at the ordinary temperature, the measurement of the oil in the receiving flask will correctly indicate the amount of oil delivered through the aperture. The conditions are altered, however, when high temperatures are required, since the oil in running in a fine stream through the orifice is chilled in contact with the air, and if its temperature be taken at the moment its volume is read in the receiving flask, a notable difference is indicated, depending upon the temperature of the room and of the oil before delivery.

In this instrument provision is made for reading the volume of

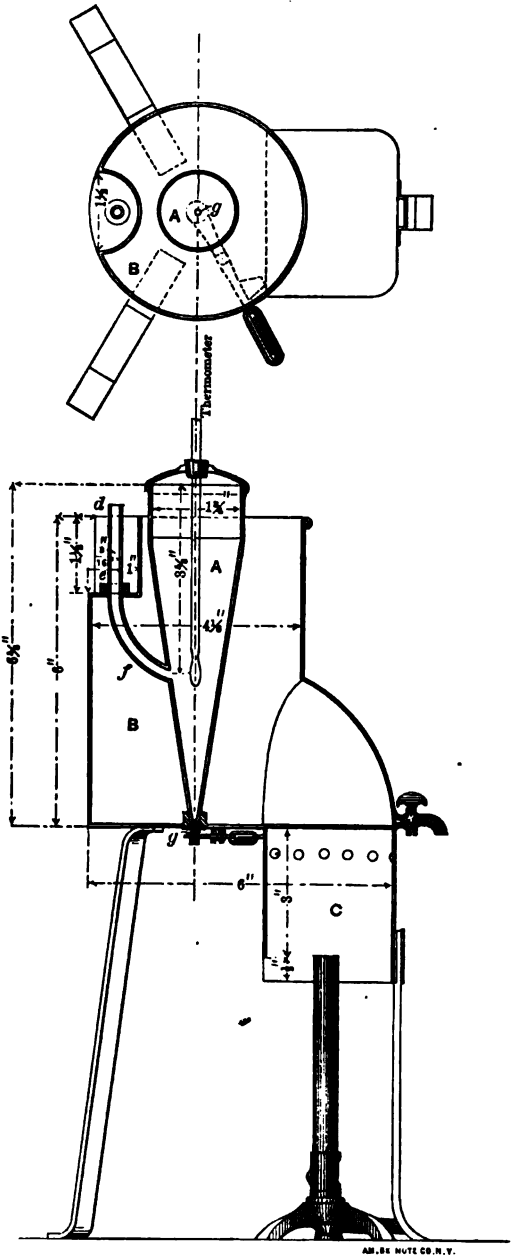


FIG. 15.

the oil directly in the chamber *A* without any graduated receiving flask, as follows:

The tube *fed* is graduated so that when the oil in the vessel *A* is at the proper level, the oil also reaches the upper graduated mark upon the tube *de*. The lower graduated mark upon the tube indicates when 25 cc. of the oil has been delivered from *A* through the orifice *g*.

This graduation is absolutely correct for the purpose, and shows accurately the viscosity of the oil at any temperature, as indicated by the thermometer in *A*.

None of the oil in tube from *e* to *d* passes into *A* during the delivery of the 25 cc. through *g*, since the tube *fed* is only partially emptied of its oil; the level of the oil in *A*, after the delivery of the 25 cc. still remaining above the point where the tube *f* enters *A*.

Second.—Oftentimes the samples of oil sent for examination do not exceed 100 cc. in bulk, an amount entirely too small if other tests are to be included.

Many forms of viscosimeters require 100 cc. of oil for the viscosity test, and not a few 50 cc.

I have found 25 cc. to be ample, provided the aperture at *g* is small enough to prevent a too rapid delivery of the oil and consequently render close readings and comparisons difficult. By making this orifice $\frac{3}{64}$ of an inch, sufficient time is secured to obtain accurate results.

If the operator prefers not to use the graduated tube *fed* to measure the oil, a receiving flask, properly marked, can be placed under *g*, as in other forms of viscosimeters.

The plan suggested by Schubler (see page 315), that viscosities should be comparable with water is the only proper one, and in the following determinations of viscosity in my laboratory the comparison is included.

	Seconds at 20° C. = 68° F.	Seconds at 50° C. = 122° F.	Seconds at 100° C. = 212° F.	Seconds at 150° C. = 302° F.	Seconds at 200° C. = 392° F.	Viscosity com- parable with Water at 20° C.
Water	15					
Prime lard oil	55	29	19	16		3.6
No. 1 " "	70	30	18	16		4.6
XXX " "	73	31	18	16		4.8
Prime Neat's-foot oil	60	28	18	19		4.0
White " "	70	28	18	16		4.6
Pure hoof oil	72	30	19	16		4.8
Oleo oil	200	30	19	16		13.3
Horse oil	64	35	17	16		4.2
Gelatine oil				360	35	
Rosin oil, 1st run	240	80	19	15		1.6
" " 2d "	70	23	15	14		4.6
" " 3d "	75	22	15	14		5.0
Dog-fish oil (Pacific)	50	26	17	16		3.0
Right whale oil (Pacific)	58	27	18	15	15	3.8
Natural bow head oil (Pacific)	47	27	18	16		3.1
Bleached whale oil "	52	27	18	16		3.4
Natural winter (Pacific) }	33	22	16	15		2.2
Sperm oil						
Bl'ch'd wintersperm oil (Pacific)	29	22	16	15		1.9
Natural spring sperm oil	30	22	17	16	15	2.0
Bleached spring sperm oil	32	22	16	15		2.1
Natural winter whale (Atlantic)	53	26	17	16		3.5
Bleached " "	53	26	18	15		3.5
Extra bleached winter whale (Atlantic)	55	28	18	16		3.6
Natural spring whale (Atlantic)	57	26	18	16		3.8
Bleached spring whale	52	26	18	16		3.4
Porpoise head oil	34	30	16	15		2.2
Sea elephant oil	51	36	17	16		3.4
Bank oil	39	30	17	16		2.6
Prime crude Menhaden oil	39	24	17	16		2.6
Brown strained " "	42	24	18	16		2.8
Light " " "	40	24	17	16		2.6
Natural winter Menhaden oil	41	25	17	16		2.7
Bleached " " "	34	24	17	16		2.2
Extra bleached winter white Menhaden oil	39	24	17	16		2.6
Castor oil	730	95	23	17	15	48.6
" White seal " castor blown oil	1170	185	28	20	20	78.0
Prime quality summer white cotton seed oil	51	26	27	15		3.4
Prime quality winter white cot- ton seed oil	57	27	18	15		3.8
Herring oil (Pacific)	56	26	18	16		3.7
Rape oil	71	26	20	16	15	4.2
Olive oil	63	24	18	16	15	4.7
" Degras " oil	205	50	20	18	15	13.6

A chart of a few of the above oils is shown in the accompanying cut (Fig. 16).

An examination of these tables and curves brings prominently forward the following facts :

That at high temperatures the variation in the viscosity of simple oils is very slight.

That "blown" oils, and "gelatine oils," which are manufactured especially to give "body" to compounded oils, fail in their purpose at high temperatures.

This is shown especially in Fig. 16, by the curves of the compounded oils—gelatine oil, for instance—which at 20 degrees C. remains solid, likewise at 50 degrees C. and 100 degrees C., but at 150 degrees C. (302 degrees Fahr.) it indicates a viscosity of 360 seconds, and at 200 degrees C. a viscosity of 35 seconds.

This "gelatine" oil is usually a compound of aluminum oleate, lard and petroleum.

Castor oil shows the highest variation of any of the simple oils, while sperm oil shows the least, and it is probably this property of the latter that has given it the reputation as a standard oil in lubrication.

Of the animal oils, "prime" lard oil ranks first in lubrication, followed in order by neat's-foot, horse oil and tallow oil.

The order of value of the marine oils would be sperm oil, porpoise head oil, bleached Menhaden, whale oil, dog fish oil, sea elephant oil, and herring oil. Of the vegetable oils, rape oil is the recognized standard in lubrication. Its use for this purpose is very limited in this country, though in Germany and Russia large amounts are annually consumed.

Olive oil, though a good lubricant, is too high in price, and its place has been taken in later years by refined cotton-seed oil. This latter oil, while seldom used alone in lubrication, is added to lard oil in proportions varying from 20 to 50 per cent., producing a mixture that lubricates nearly as well as pure lard oil, though acidity more rapidly develops than in lard oil alone. Castor oil is largely added to other oils to give high viscosity at ordinary temperatures, and to produce "body," which it loses at high temperatures. Its use for this purpose still continues in England, while in this country "gelatine" oil has largely taken its place, and produces a more viscid oil at less expense.

The so-called "seal castors" and "blown oils" are made from

cotton-seed oil and castor oil, and are used in place of "gelatine" oil to produce high viscosity, at a much lower cost than "gelatine" oil.

The *compounded oils*, as now made for lubrication, show that the manufacturer considers the best selling oil to be one which has a high viscosity at ordinary temperatures, and that in many cases this property has been added to the oil by the use of thickening compounds.

Consult the following :

JOUR. ANAL. CHEM. 1, 150.

Analyse der Fette und Wachsarten, Benedict, p. 45.

Ding. Poly. Jour. 261, 81; 259, 270; 260, 282; 261, 311.

Portefeuille Economique de Machines, 1886, 2, 206.

Berichte 267, 592.

Mitth. der Tech. Versuchsanstalten, 1888, 3, 8.

Ding. Poly. Jour. 279, 113.

Chem. Zeit., 1891, p. 298.

Oils and Varnishes, Cameron, p. 303.

Zeit. f. anal. Chem. 20, 465.

Zeit. des Vereins Deutscher Ingenieure 31, 251.

Jour. Soc. Chem. Ind. 4, 77; 5, 121; 5, 360; 6, 414; 10, 617.

The Railroad and Engineering Journal 64, 224.

Mitt. Konig. tech. Versuchs, 1890, p. 143.

Chem. Zeit. 7, 763.

The Engineer, 1890, p. 305.

Zeit. f. anal. Chem. 27, 528.

IODINE ABSORPTION.

The determination of the iodine absorption of an oil is probably the most important chemical test for recognition quantitatively in a mixture of oils.

Introduced by Hübl (*Ding. Poly. Journ.*, 253, 281), it has since maintained this position, though other chemists have introduced the bromine absorption and others of similar character. They have not been adopted with the confidence of the iodine process.

Warren (*Chem. News* 56, 188) draws attention to the fact that Chateau in his *Essais Personnelles*, p. 70, used the iodine absorption in a manner similar to Hübl many years previously.

The directions for testing oils by this method are given very

completely in *Analyse der Fetten Oele und Wachsarten*, Benedikt, p. 74, and in *Oils and Varnishes*, Cameron, p. 248.

In a mixture of two fatty oils with a mineral oil, the best results are obtained by saponifying and separating the fatty acids from the mineral oil. The iodine absorption of the mixed fatty acids is then taken, and where the nature of them has already been shown by color tests, etc., their proportion can be indicated by the following formula :

$$x = \frac{100 (I - n)}{m - n}$$

Where x = the percentage of one fat,
 y = " " the other,
 I = iodine degree of mixture,
 m = " " fat x ,
 n = " " " y .

If more than two fatty oils are present in a mixture with mineral oil, the method of Warren (*Chem. News* 62, 215 ; *JOUR. ANAL. AND APPLIED CHEM.* 5, 215) can be used.

The following determinations of the iodine absorption made in my laboratory are indicative of the variations of the absorption by the different oils :

Prime lard oil	76.4	77.2
No. 1 "	69.8	69.9
XXX "	65.1	65.6
Oleo oil	51.6	51.6
Prime Neatsfoot oil	80.1	82.0
Horse oil	82.3	82.5
Natural bow-head whale oil	130.5	131.1
" winter "	121.1	126.0
Extra bleached winter "	124.9	126.1
Bleached spring "	126.1	126.2
Crude sperm oil	82.3	82.3
Prime quality winter white cotton-seed oil	114.2	114.9
Olive oil	81.	
Prime quality summer white cotton-seed oil	110.2	110.6
" winter yellow " "	115.9	118.6
" summer " " "	104.0	104.4
Herring oil	122.1	123.8
Dog fish oil	102.7	104.7
Porpoise-head oil	28.9	29.1
Rosin oil, second run	92.1	93.4
" third "	90.4	92.2

References.

- E. J. Mills and James Snodgrass (*Jour. Soc. Chem. Ind.* **2**, 435).
 L. Archbutt (*Jour. Soc. Chem. Ind.* **5**, 303).
 A. H. Allen (*Jour. Soc. Chem. Ind.* **5**, 65).
 E. Dieterich (*Pharm. Centralhalle* **8**, 570).
 R. Williams (*Chem. Zeit. Rep.* **12**, 127; *Jour. Anal. Chem.* **3**, 454).
 R. H. Thomson and H. Ballantyne (*Jour. Soc. Chem. Ind.* **9**, 588).
 R. M. Moore (*Jour. Amer. Chem. Soc.* **11**, 155).
 T. B. Warren (*Chem. News* **62**, 27; *JOUR. ANAL. AND APPLIED CHEM.* **5**, 111).
 Reuben Haines (*JOUR. ANAL. AND APPLIED CHEM.* **5**, 289).
 O. Schweissinger and R. Marzahn (*Pharm. Centralhalle* **28**, 146).
 Benedikt (*Ztschr. f. d. Chem. Industrie*, 1887, heft 8).
 Stillman (*The Stevens Indicator*, **6**, 202; *JOUR. ANAL. AND APPLIED CHEM.* **3**, 365).
 O. Schweissinger and R. Marzahn (*Pharm. Centralhalle* **28**, 146).
 Benedikt (*Ztschr. f. d. Chem. Industrie*, 1887, heft 8).
 Bruno Rose (*Repert der Anal. Chemie* **6**, 685).
 F. W. A. Woll (*Ztschr. Anal. Chem.* **27**, 532).
 Ch. Dubois and L. Padi (*Bull. Soc. Chem. de Paris* **43**, 207).
 A. Von Asboth (*Chem. Zeit.* **14**, 825).
 L. de Koninck (*Ned. Tijdschr. von Pharm.*, 1890, 22).

LARD OIL.

Sp. gr. .915; cold test, 7 degrees C.; viscosity at 20 degrees C., 3.6; Maumene's test, 40 degrees C.; iodine absorption, 66.

Adulterants.—Tallow oil, cotton-seed oil, paraffin oil, rosin oil. The best engine oil is a mixture of lard oil and paraffin oil in equal parts. This compound has been in use by the P. R. R. for the past ten years, and after many experiments and trials of different substitutes, still remains the standard.

Passenger car oil is usually a mixture of well oil and lard oil in the proportion of two-thirds well oil and one-third lard oil. Lard oil in the proportion of one part to three of "500° well oil" has been found to give the best results as a cylinder lubricator (Dudley, *The Railroad and Engineering Journal* **64**, 73-126).

NEATS-FOOT OIL.

Sp. gr. .915; cold test, 4 degrees C.; viscosity at 20 degrees C. = 4; Maumene's test = 40 degrees C.; iodine absorption, 80.

Adulterants.—Same as for lard oil; also cheap grade of olive oil. Schaedler states light colored whale oils are often used, and poor grades of lard oil.

References.

- The Chemical News* 42, 27.
Moniteur Scientifique Quesneville, April, 1880.
Oils and Varnishes. Cameron, p. 20.
Handwörterbuch der Tech. Chem. Böttger and Gräger, p. 252.
The Railroad and Engineering Journal 64, 73.
Die Fetten Oelen. Dr. George Bornemann, p. 285.

THE MARINE OILS.

References.

- Commercial Products of the Sea.* P. L. Simond.
Animal and Vegetable Fats and Oils. W. T. Brannt.
The Fish Industries of the United States. E. Brown Goode.
Spons' Encyclopedia of the Arts and Sciences.
The Oil, Paint and Drug Reporter.
Die Technologie der Fette und Oele. W. Carl Schaedler.

"DEGRAS OIL."

The degras is a product of tanning skins in oil and chemicals, and is practically an emulsion or weak soap, unless the alkali has been set free by weak acid treatment and the moisture boiled out.

The French make is called "Degras," and practically the same class of oil in England goes by the name of "sod oil."

In the United States "wool-grease" is often called "Degras." It, however, contains no fish oil as does Degras.

In lubrication it is made use of by mixing it with mineral oil in the proportion of 10 per cent. of Degras to 90 per cent. of the mineral oil.

At normal temperature it forms a good lubricant for special purposes, but often froths at high temperatures owing to the water and soap present.

The composition of "Degras" varies greatly, as the following analyses by Jean (*Moniteur Scientifique* 15, 889) show :

	I.	III.
Water	18.90	12.93
Ash	0.25	0.55
Oil	69.71	80.00
Unsaponifiable matter	6.84	. .
Resinous substances	4.00	5.81

Consult also—

Benedikt (*Untersuchung von Producten der Fett Industrie*, p. 157).

Brandt (*Animal and Vegetable Fats and Oils*).

H. W. Langbeck (*Jour. Soc. Chem. Ind.* **10**; *JOUR. ANAL. AND APPLIED CHEM.* **5**, 169).

OLIVE OIL.

Sp. gr. .916; cold test, 2 to 6 degrees C.; viscosity at 20 degrees C., 4.2; Maumene's test, 42 degrees C.; iodine absorption of oil, 81.

References.

G. A. Buchheirte (*Jour. Soc. Chem. Ind.* **1**, 32).

M. Seechim (*Jour. Soc. Chem. Ind.* **1**, 237).

T. Leone (*Gazz. Chim. ital.* 1889, p. 355).

M. Zecchini (*Berichte der d. chem. Gesell.* **15**, 1220).

Souchère (*Moniteur scient.* **11**, 791).

C. B. Dudley and F. N. Pease (*The Railroad and Engineering Journal* **64**, 76).

O. Bach (*Chem. Zeit.* **7**, 356; *Zeit. für anal. Chem.* **28**, 259).

Dr. Geo. Bornemann (*Die Fetten Oelen*, p. 247).

Milliau (*Compt. rend.* **106**, 530; *JOUR. ANAL. CHEM.* **2**, 200).

H. Levy (*Chem. Zeit. Rep.* **12**, 238).

E. Hirschsohn (*Chem. Zeit. Rep.* **12**, 341).

Legler (*Chem. Zeit.* **8**, 1657).

J. Birl (*Archiv der Pharmacie* **225**, 310).

A. Andoynaud (*Compt. Rend.* **101**, 752).

E. Bechi (*Chem. Zeit.* **11**, 1328; *The Analyst* **11**, 171).

L. Archbutt (*Jour. Soc. Chem. Ind.* **8**, 685).

L. A. Bernays (*The Manufacture of Olive Oil*).

COTTON-SEED OIL.

Sp. gr. .921-.927; cold test, —9 degrees C.; viscosity at 20 degrees C. = 3.8; Maumene's test, 75 degrees C.; iodine absorption of oil, 110-118.

References.

- B. Nickell (*J. Chem. Soc.* **38**, 925).
J. Macagno (*Gazz. Chim.*, 1881, p. 223).
E. Bechi (*Chem. Zeit.* **11**, 1328).
E. Millau (*Mont. Scient.* 1888, 366).
H. Levy (*Chem. Zeit. Rep.* **12**, 238).
E. Hirschsohn (*Chem. Zeit. Rep.* **12**, 341).
T. Leone (*Gazz. Chim. ital.*, 1889, p. 355).
J. Conroy (*Ztschr. für anal. Chem.* **22**, 289).
Bradford, S. S. (*Ztschr. für anal. Chem.* **27**, 528).
Lavallois (*Chem. Zeit.* **11**, 53).
A. C. J. Charlier (*The Engineer*, 1890, p. 305).
T. Leone and A. Longi (*Gazz. Chim.* **16**, 393).

The oils made use of in lubrication can be separated into two groups—saponifiable and unsaponifiable. To the former belong all the fatty oils; to the latter the mineral and rosin oils.

The method of Lux (*Zeit. f. anal. Chem.* **24**, 347) is made use of to determine if any fatty oils are present in a mineral oil.

If rosin oil is suspected to have been added to the mineral, it can be identified by the method of Holde (*Mittheil der König. tech. Versuchsanstalten*, 1890, p. 19), or the process of E. Valenta (*Zeit. für anal. Chem.* **25**, 441) can be used.

These three tests will indicate, qualitatively, the presence of any fatty or rosin oil in a mineral oil. It is rarely, in the better class of lubricating oils, that more than one oil is added to a mineral oil, such, for instance, as lard oil, or whale oil, in which case saponification easily separates the two oils, and identification of each by special tests can then be made.

When, however, the oil added to the mineral oil itself contains an adulterant, such as lard oil to which cotton-seed oil has been added, then the fatty acids separated by saponification will require a more extended examination to prove the presence of both lard oil and cotton-seed oil.

For the method of saponification and separation of a fatty oil from a mineral oil, consult Benedikt (*Analyse der Fette und Wacharten*, p. 91).

The following skeleton scheme is given to show the application of the above upon a lubricating oil that qualitative analysis has

shown to contain mineral oil, lard oil, cotton-seed oil and rosin oil.

20 gms. of the oil are weighed out in a No. 3 beaker. 100 cc. of an alcoholic solution of potash (80 gms. KHO to 1000 cc. alcohol 98 per cent.) are added, and heat applied with stirring until the alcohol is all driven off; add 100 cc. H₂O, heat with agitation, cool, add 50 cc. ether, transfer to separatory funnel, stopper, shake well, and allow to stand 6 hours. Draw off the soap solution.

1. *Soap solution* (contains the fatty acids of the lard and cotton-seed oils).

Heat 10 minutes nearly to boiling, cool, acidify with dilute H₂SO₄; allow to stand a few hours; collect the separated fatty acids; determine their weight, then test as follows:

1st portion.—Determine the "melting point." Consult, *Analyse der Fette und Wacharten*, Benedikt, p. 181.

2d portion.—Determine the "Iodine absorption" and their rates by formula,

$$x = \frac{100 (I - n)}{m - n}$$

Consult, *Oils and Varnishes*, Cameron, p. 248.

3d portion.—Determine the "Saponification equivalent." Consult, *Oils and Varnishes*, Cameron, p. 246.

These three determinations will give the proportion of fatty acids belonging to the lard oil and to the cotton-seed oil.

Having these, the amount of the oils corresponding to their fatty acids are calculated. Consult, Benedikt, p. 138.

(2) *Ether solution* remaining in the separatory funnel is transferred to a flask, the ether distilled, and the mineral and rosin oils weighed together, and then treated by *Twitcheil's* process, for the determination of rosin in oils (JOUR. ANAL. AND APPLIED. CHEM. 5, 379), or by H. Demski and Th. Morawski's method for the estimation of rosin oil in mineral oils (*Ztschr. f. anal. Chem.* 28, 124; *Ding. Poly. Jour.* 258, 82).

Having subtracted the weight of the rosin oil thus found from the weight of the mixture of mineral and rosin oils, the residue is the amount of mineral oil.

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Resins and Fatty Oils and Heavy Mineral Oils in Oils of Commerce (*Chem. News* 42, 39).

Separation of Hydrocarbon Oils from Fat Oils (*Chem. News* 44, 161).

Estimation of Undecomposed Fats in Mixture of Fatty Acids (*Chem. News* 47, 72).

Determination of Free Fatty Acids in Oils (*Chem. News* 48, 48).

- Determination of Cotton-seed Oil in Olive Oil (*Chem. News* **49**, 49).
Examination of Mineral Oils (*Chem. News* **51**, 69).
A New Agent for Thickening Mineral Lubricating Oils (*Chem. News* **58**, 299).
On the Detection of Adulterations in Oils (*Chem. News* **58**, 292).
Determination of Mineral Oils (*Chem. News* **57**, 81).
Blown Oil (*Chem. News* **58**, 170).
New Method of Examining Mixture of Lard and Olive Oils (*Chem. News* **58**, 15).
Process for Proving Rosin Oil (*Ding. Poly. Jour.* **258**, 94).
Foeke's Method for Mineral Oils and Fats (*Ding. Poly. Jour.* **259**, 146).
Examination of Mineral Lubricating Oils for Other Oils (*Ding. Poly. Jour.* **286**, 487).
Estimation of Rosin in Oils and Fats (*Ber. d. deut. chem. Gesell.* **15**, 965).
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Melting Points of Fatty Acids of Olive Oil, Cotton-seed Oil, etc. (*Gazz. Chem.* **16**).
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The Detection of Rosin Oil in Castor Oil (*Jour. Soc. Chem. Ind.* **10**).
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Adulteration of Oils. Lard Oil with Cocoanut Oil. etc. (*Amer. Chem. Jour.* 1886.)
Lard Oil in Olive Oil (*Chem. News* **58**, 15).
Testing and Reporting upon Lubricating Oils (*Chem. News* **55**, 203).
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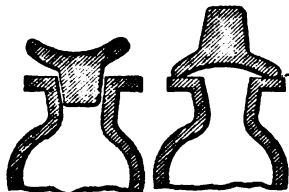


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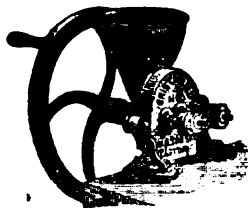
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